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ROOM TEMPERATURE CURING RESIN SYSTEMS FOR GRAPHITE/EPOXY COMPOS--ETC(U)
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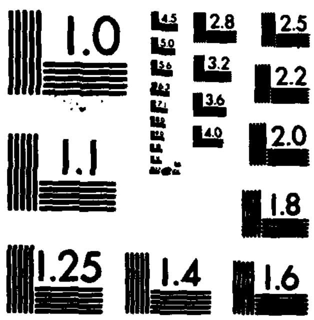

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Adhesive formulations were developed for the repair of damaged graphite/epoxy structures on board ship. These adhesives cure at 24C (75F) or in the moderate temperature range of 67 to 121C (150 to 250F). The formulations which gave the best results in lap shear testing were formulated from high molecular weight and high functionality epoxy resins and a polyamine curing agent. A typical formulation is composed of a cresol novalac epoxy, (Ciba-Geigy ECN 1299), the triglycidyl ether of p-aminophenol, (Ciba-Geigy 0510), →

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and diethylenetriamine, a polyamine curing agent. After a 72 hour cure at 24C (75F) an adhesive compounded from this formulation had much higher lap shear strength at 121C (250F) than did commercially available epoxy, acrylic, and anaerobic adhesives. Aluminum/aluminum bonds tested in a rapid heat-up to 121C (250F) (at 150F/min) and immediate application of load at 121C (250F) had lap shear strength of 1400 psi whereas the commercial adhesives had 500-700 psi strength in the same test. The formulation when cured at 121C (250F) had lap shear strength at 121C (250F) of 2700 psi. Another promising system is the vinyl ester resin system as a moderate temperature, 66C to 121C (150F to 250F), curing adhesive. It has good environmental durability.

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SECTION 1

INTRODUCTION AND SUMMARY

Now that graphite fiber/epoxy resin composite structures are being used on production Naval aircraft it is essential to develop reliable methods of repairing these structures when they are damaged. Major cost reductions in repair could be realized and a higher utilization of aircraft during a national emergency could be achieved if very simple, rapid, and inexpensive repairs could be made on board ships operating at sea. To make these repairs possible, low temperature or moderate temperature curing resins and adhesives must be developed. The cure of these resins must not require the use of large, expensive, and complex types of equipment that are difficult or impossible to maintain or are unavailable on board ship. In the ideal situation no heat at all should be used for the cure of the resins used in repair. However, the development of moderate temperature curing resins that fully cure in short periods of time (e.g., 30 minutes at 66C (150F) to 121C (250F) will be a major advance for repair. At the present time there are no ambient temperature or moderate temperature curing resins that satisfy the stringent requirements demanded of resins used for repair of aircraft structures. Resin systems that can meet these requirements must be developed. The ambient temperature range in which the adhesives would be cured is from 10C to 38C (50F to 100F).

The primary goal of this program has been to develop 24C (75F) temperature curing polymer systems which can be formulated into adhesives for repairing damaged graphite/epoxy composite aircraft structures in the difficult working conditions found on board ship. For a 24C (75F) temperature curing adhesive to be truly practical a bonded joint prepared from it must be capable of carrying its full design load at the maximum temperature of exposure within 1 to 4 hours after preparation without using any heat to accelerate or to complete the cure. This represents the case where a damaged airplane is repaired with an adhesive cured at 24C (75F) and four hours after the repair has been completed the plane is flown. During flight the repair patch experiences aerodynamic loading and heating. The 24C (75F) curing adhesives that are commercially available cannot survive these conditions.

Lap shear bonds made from these adhesives when exposed to aerodynamic heating (250F) cannot carry high stress unless postcured. To simulate the effect of aerodynamic heating, the bonds are rapidly heated to 250F (heat-up rates are typically 50F/min to 100F/minute) and loaded as soon as the bond reaches 250F.

A secondary goal of this program has been to develop an adhesive which would cure rapidly at moderate temperatures and which would be very easy to use in the field. Cure within 30 minutes at a temperature of 66C (150F) is very desirable. The goal is a cure within 60 minutes at 121C (250F) or lower.

Of course there are excellent thermal curing epoxy structural adhesives commercially available. But these adhesives were designed for autoclave cure. In order to realize their high adhesive properties they must be cured with complex cure cycles using high pressures (for example, 40 psi) and temperatures as high as 177C (350F). Factors in the cure cycle which are critical are the heat-up rate, the temperature at which vacuum is applied, the temperature at which vacuum is vented, and the total pressure. In addition the temperature and the humidity of the room in which the adhesive is used are critically important, and the adhesive must be kept in refrigerated storage.

Significant progress has been made in this program in developing both improved 24C (75F) curing and moderate temperature curing adhesives. Using the heating and loading conditions described (very rapid heat-up to 250F and immediate application of load) the 24C (75F) temperature curing adhesives developed in this program had lap shear tensile strength in the range 1200 to 1900 psi at 121C (250F) whereas the commercial adhesives had strengths well below 1000 psi. Several polymer systems were identified which show considerable promise for adhesives which cure rapidly at moderate temperatures.

The results obtained with commercial ambient temperature curing adhesives are listed in Table 1. The results obtained with the 24C (75F) curing adhesives developed in this program are listed in Table 2.

The adhesive systems which were developed in this program were prepared from commercially available polymers which were modified to meet the requirements of the program. The synthesis of new polymers was not in the scope of the program. Four polymeric systems were investigated: epoxies were selected because they give the best combination of mechanical and adhesive properties

and they can be cured at low temperatures with a wide variety of curing agents; vinyl esters were selected because they are readily cured at low temperatures and have good environmental durability; reactive acrylics and anaerobics were selected because they cure readily at low temperatures and are known to have good adhesive properties.

Table 1. Lap Shear Tensile Strength of Commercial Adhesives
Lap Shear Bonds Cured 72 Hours at 24C (75F)

Lap Shear Panels: 7075-T6 Aluminum With BAC 5555 Surface Treatment

Adhesive Identification	Adhesive Type	Manufacturer	Lap Shear Tensile Strength @ 24C (77F), psi	*Lap Shear Tensile Strength @ 121C (250F), psi
Quickbond 610	Anaerobic	Permabond	2770	420
Multibond 33038	Anaerobic	Loctite	1780	100
4173	Anaerobic	3M	580	-
Sumikatite H200	Anaerobic	Sumitomo	360	-
Sumikatite H300	Anaerobic	Sumitomo	340	-
Speedbonder 306	Anaerobic	Loctite	1420	600
Speedbonder 324	Anaerobic	Loctite	2720	300
Speedbonder 325	Anaerobic	Loctite	1590	460
EA 9446	Acrylic	Hysol	2060	320
RA 0018	Acrylic	Fuller	3020	730
RP 5613	Acrylic	REN	1600	490
A 1177	Acrylic	Goodrich	1290	360
M890	Acrylic	Bostic-Finch	3760	390
Rexite IMR-P2	Acrylic	Franklin	3720	760
Versilok 513	Acrylic	Beacon	2570	340
Weldmaster 3	Acrylic	National	4170	560
Epoxylite 203	Epoxy	Epoxylite	1400	460
RP-138	Epoxy	REN	1470	370

*Test conditions: Rapid heat up to 121C (250F) apply load when specimen reaches 121C (250F).

Table 2. Lap Shear Tensile Strength of Epoxy Formulations Developed on this Program Lap Shear Bonds Cured at 24C (75F)

Lap Shear Panels: 7075-T6 Aluminum With BAC 5555 Surface Treatment

Adhesive Formulation*	Lap Shear Tensile Strength @ 24C (77F)	**Lap Shear Tensile Strength @ 121C (250F)
ECN 1299/0510/DETA	3620	1430
SU-8/0510/DETA	2300	1400
EPON 1031/0510/DETA	2260	1320
APOGEN 101/0510/DETA	2400	1560
ECN 1299/EPON 871/0510/DETA	3160	1560

*Resin and curing agents are identified in Tables 5 and 6.

**Test conditions: Rapid heat up to 121C (250F), apply load when specimen reaches 121C (250F)

SECTION 2

TECHNICAL DISCUSSION

2.1 BACKGROUND TO THE PROBLEM OF DEVELOPING 24C (75F) CURING ADHESIVES

The primary goal of this program is the development of a 24C (75F) temperature curing resin system which can function as a structural adhesive over a broad temperature range (-67F to 250F). Room temperature curing epoxy adhesives have been available for years; however, these adhesives, even though they solidify readily at low temperature (e.g., 75F), require postcure at some elevated temperature before they will carry loads at any temperature much above this initial cure temperature. This is because polymeric materials can solidify when only a low percentage of the reactive groups crosslink. But cure is so incomplete and the crosslink density is so low that the material will soften when heated only a few degrees.

The difficulty associated with obtaining good quality mechanical properties at elevated temperatures from a resin cured at 24C (75F) lies in the fact that "complete" cure only seems to occur while the resin is in a fluid or rubbery state. In the solid state the rate of reaction is too low for any meaningful increase in cure to occur. Therefore the resin must be cured at or above its glass transition temperature.

To illustrate this a DSC analysis (Figure 1) was made of room temperature cured Epon 828/DETA, a resin system which has been widely used as an ambient temperature adhesive for many years. The resin was cured 72 hours at 24C (75F). Note that the resin begins to soften at 35C (95F), and at 60C (140F) a cure reaction is initiated. A DSC analysis of the same resin system following ambient temperature cure and a one-hour postcure at 177C (350F) is shown in Figure 2. Note that the resin is fully cured now. There is a glass transition temperature at approximately 100C (212F) and there is no cure exotherm.

The secondary objective of this program has been the development of adhesives which cure rapidly at moderate temperatures in the range 150 to 250F. This requires the use of very reactive curing agents. Generally the more

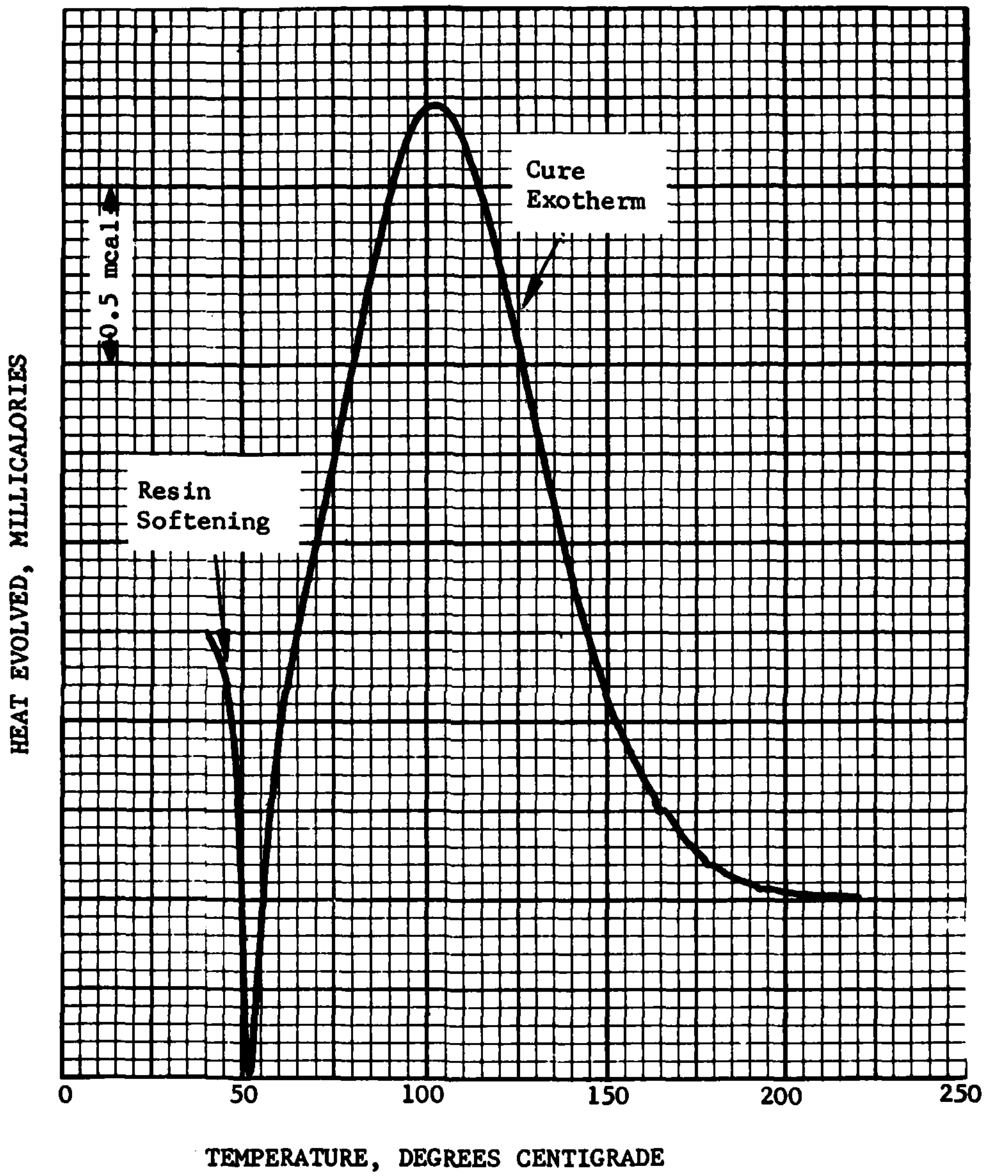


Figure 1. DSC Analysis of Epon 828/DETA After 72 Hour Cure at 24C (75F)

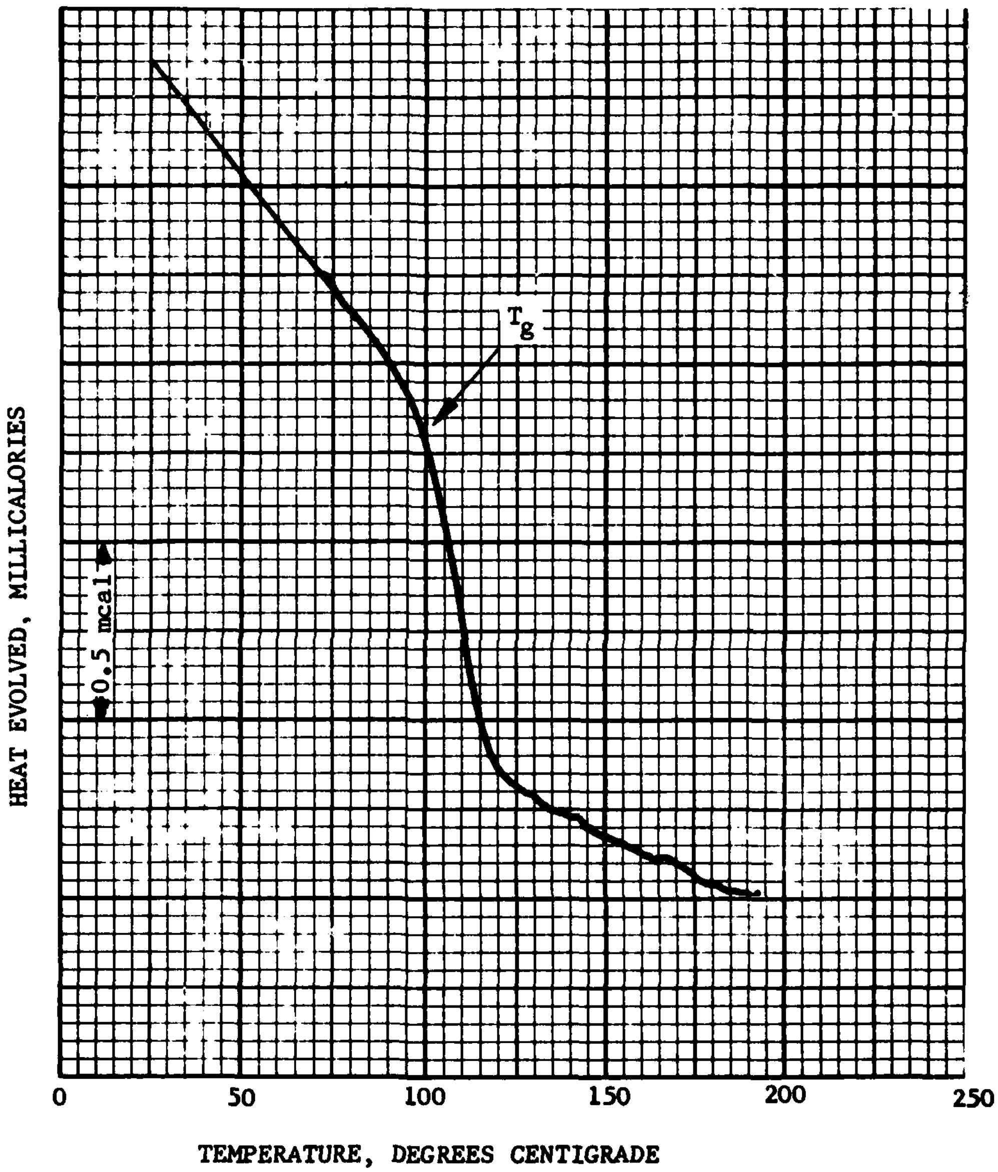


Figure 2. DSC Analysis of Epon 828/DETA After 72 Hour Cure at 24C (75F) and One Hour Postcure at 177C (350F)

reactive curing agents give lower glass transition temperatures than the less reactive curing agents.

The approach taken to achieve the goals of this program was to use high molecular weight, high functionality polymeric materials. These materials require minimum chain extension and crosslinking reactions to reach the high molecular weight and crosslink density required to function as high strength structural adhesives.

2.2 PROGRAM ADHESIVE REQUIREMENTS AND GOALS

All the polymer systems developed for this p ;ram had to meet the stringent requirements demanded of polymers used in aircraft structures. The major requirements include: (1) thermal stability, (2) environmental durability, and (3) mechanical properties. Each of these is discussed below:

(1) Thermal Stability

The polymer systems developed in this program must be capable of withstanding the temperature/time profiles of flight missions experienced by military fighter aircraft such as the U.S. Navy F-18A. In order to define the flight missions of the F-18A, days on which flights occur are divided into "standard days," "tropical days," "cold days," and "hot days." The temperature/time profiles of a flight occurring on each "day" are shown in Figures 3 through 6. As can be seen the temperature extremes range from -53C (-65F) to 99C (210F). The polymers developed in this program must be capable of functioning at least over this temperature range. To meet the upper use temperature we have selected 120C (248F) as the desired minimum glass transition temperature. The percentage of time the F-18A flies on each "day" is as follows:

tropical day	51.9%
standard day	41.8%
cold day	3.5%
hot day	2.8%

The actual time the aircraft spends at the extreme temperatures is minimal because the aircraft rarely flies on "cold" and "hot" days.

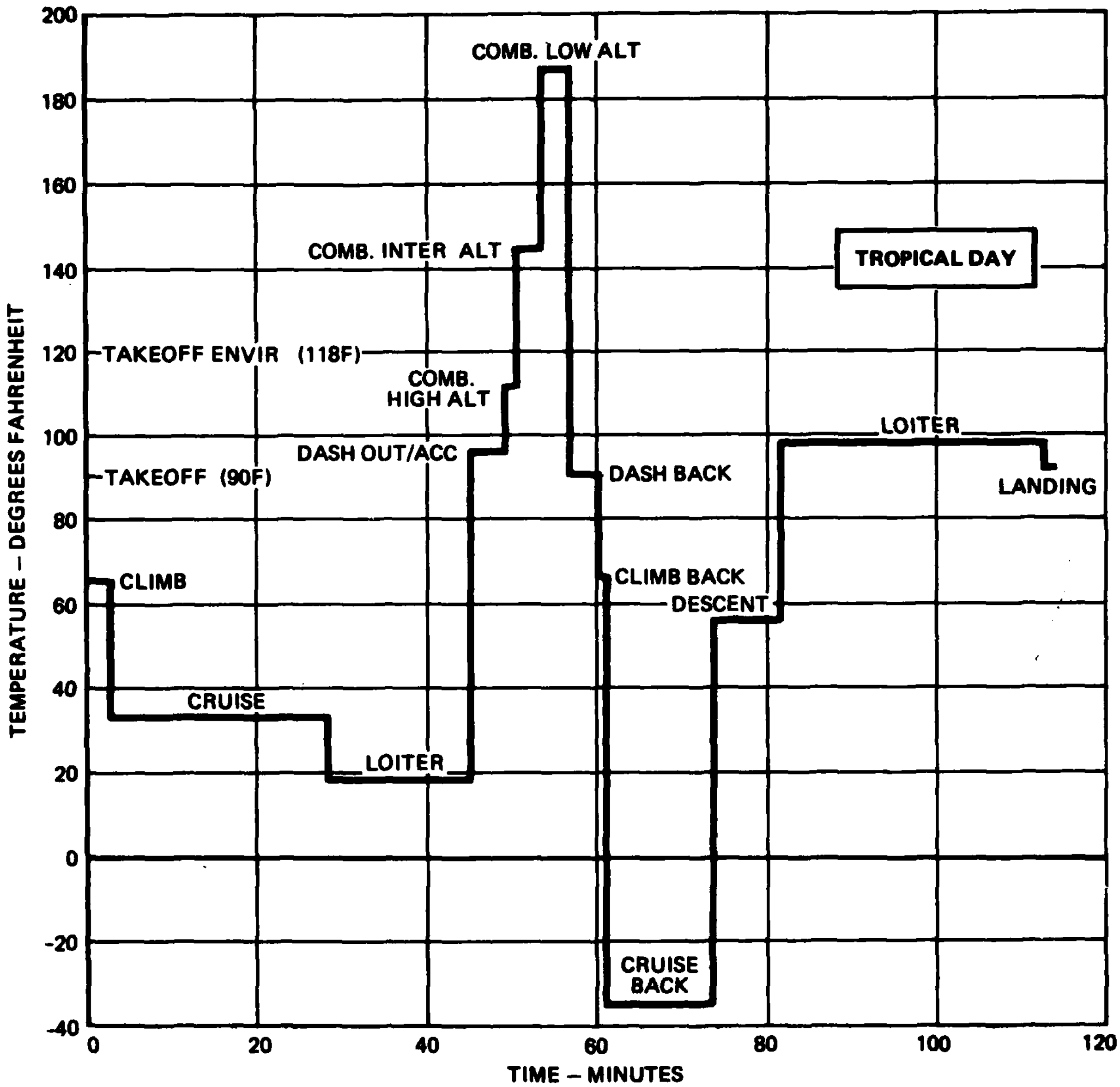


Figure 3. Temperature/Time Profile for F-18A on a "Tropical" Day

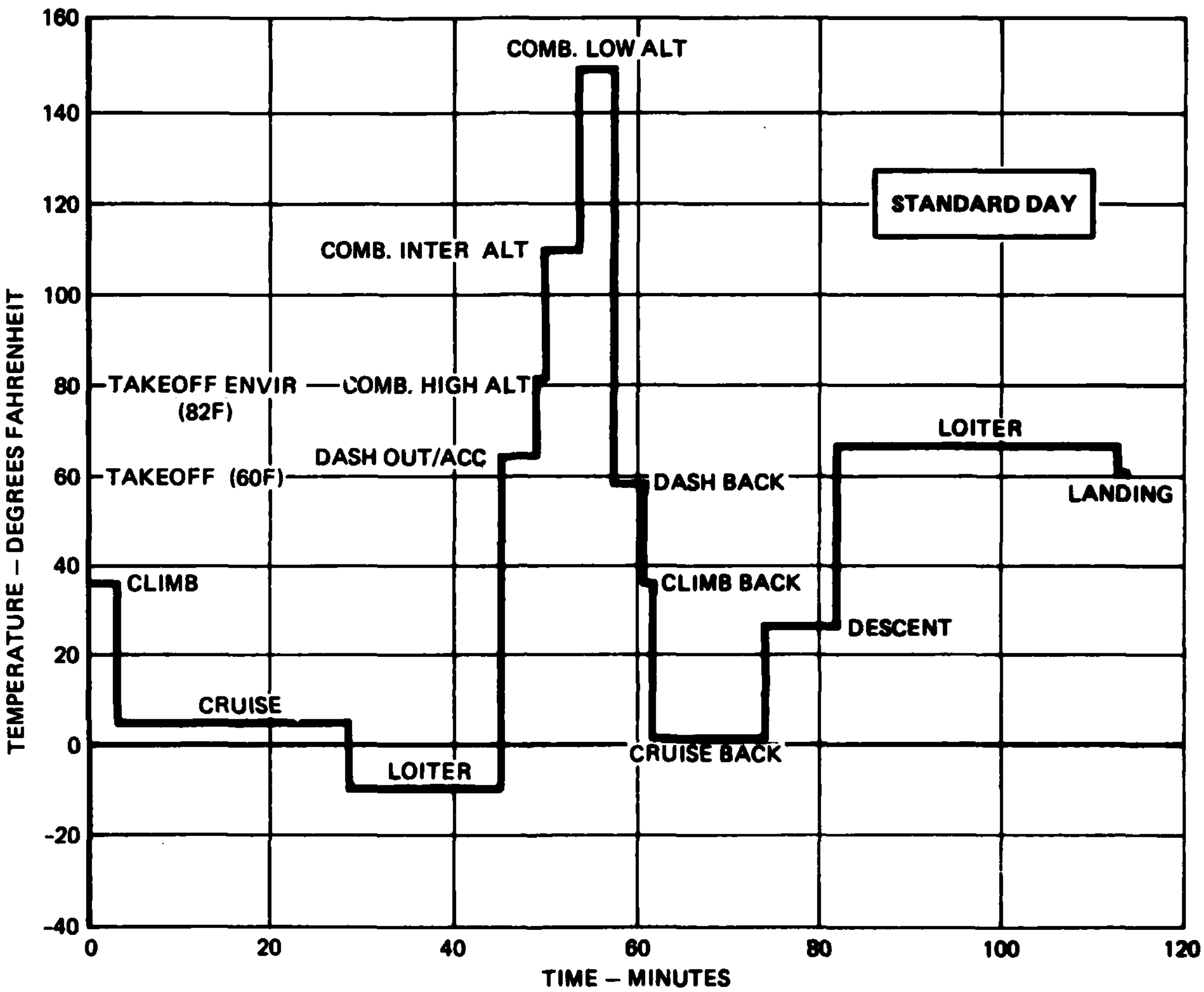


Figure 4. Temperature/Time Profile for F-18A on a "Standard" Day

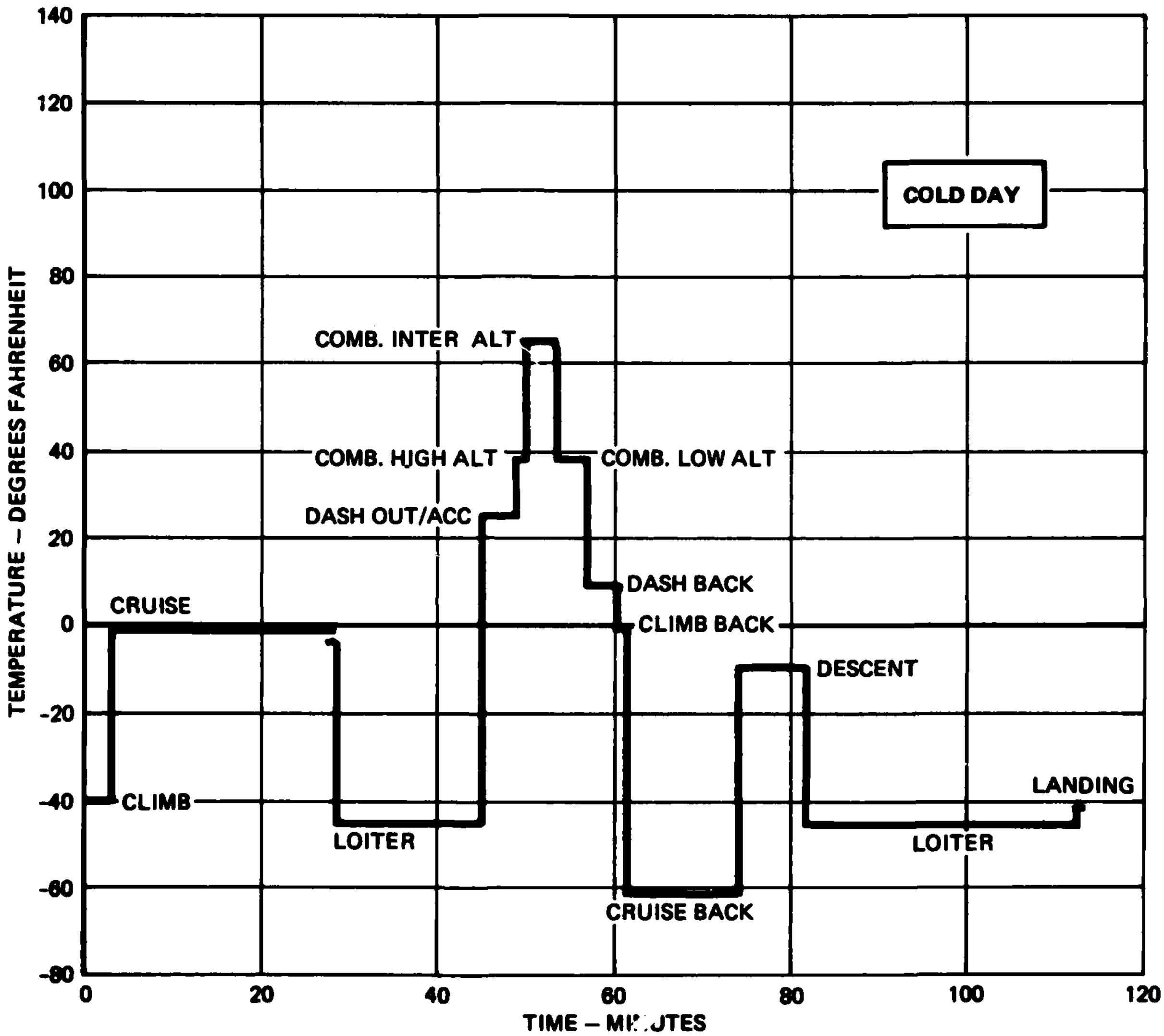


Figure 5. Temperature/Time Profile for F-18A on a "Cold" Day

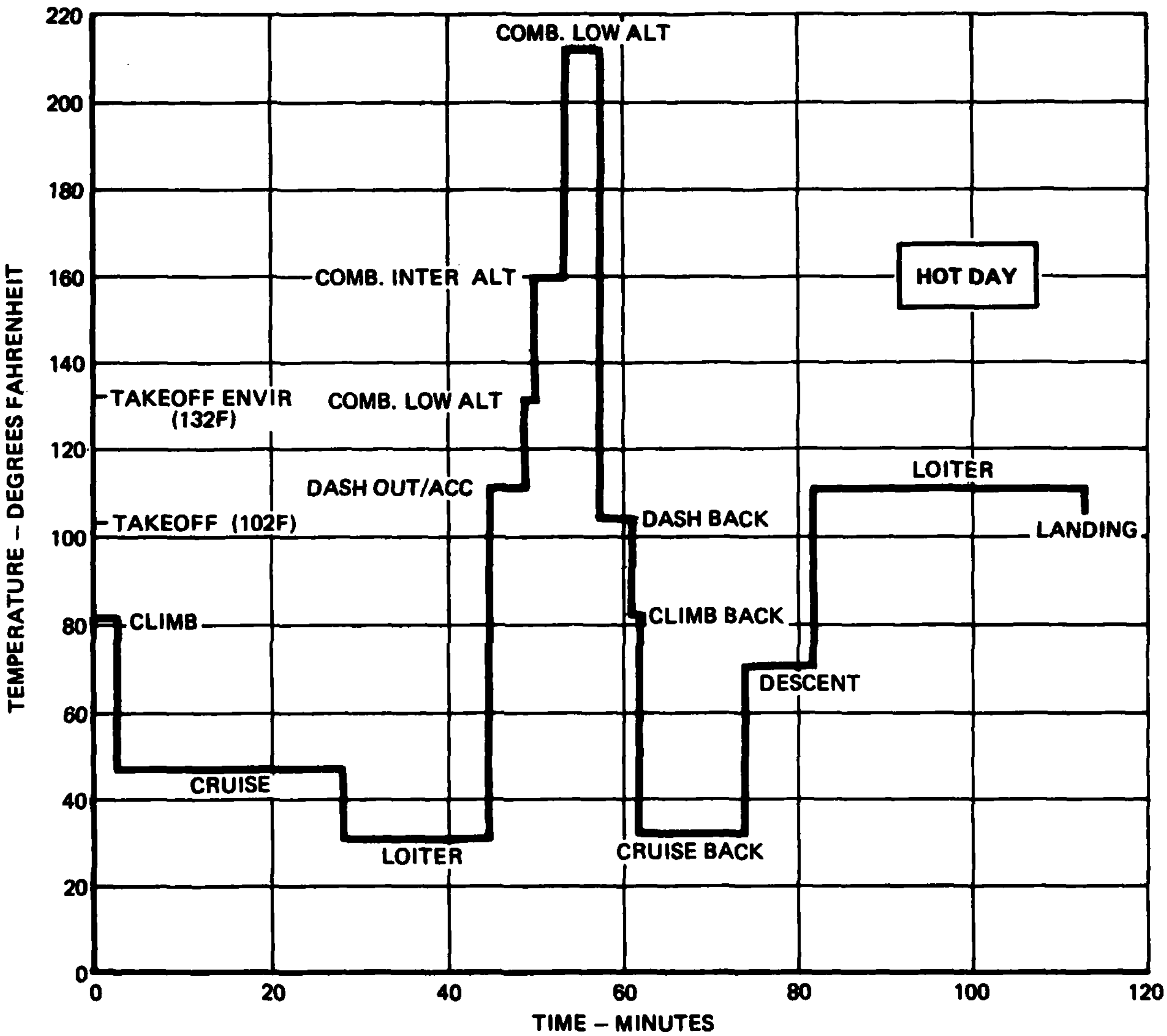


Figure 6. Temperature/Time Profile for F-18A on a "Hot" Day

(2) Environmental Durability

The polymer systems must have acceptable environmental durability to moisture, sunlight, and the various fluids encountered during the routine flight and service of aircraft. These fluids include fuel, hydraulic oils, and paint strippers. Any polymeric material used for repair must have environmental durability at least equivalent to the durability of the 3501-6 epoxy resin system because 3501-6 is used as the matrix resin in the F-18A graphite fiber composites.

(3) Mechanical Properties

The polymer systems developed in this program must have sufficient modulus, tensile strength, and fracture toughness to function as a load transfer medium in repair joints. We selected the following lap shear strengths as targets in this program:

Room temperature, dry	3000 psi minimum
121C (250F), dry	1750 psi minimum
121C (250F), wet*	1500 psi minimum

2.3 PROGRAM METHODOLOGY

The methodology used in this program is shown graphically in Figure 7. Instrumental analyses were used to determine the cure characteristics of candidate polymers. Mechanical strength data such as tensile lap shear strength and composite strength and modulus were used to evaluate polymers which instrumental analysis showed to be promising.

The following methods of analysis were used for the evaluation of polymer systems:

(1) Differential Scanning Calorimetry (DSC). DSC was used to determine temperatures at which cure occurs, the rate of cure at various temperatures, the degree of cure obtained, the melting or softening temperature of partially cured polymers, and the glass transition temperature of cured polymers.

(2) Thermomechanical Analysis (TMA). TMA was used to determine the softening temperature and glass transition temperatures of polymers.

*Adhesive with 1% moisture content.

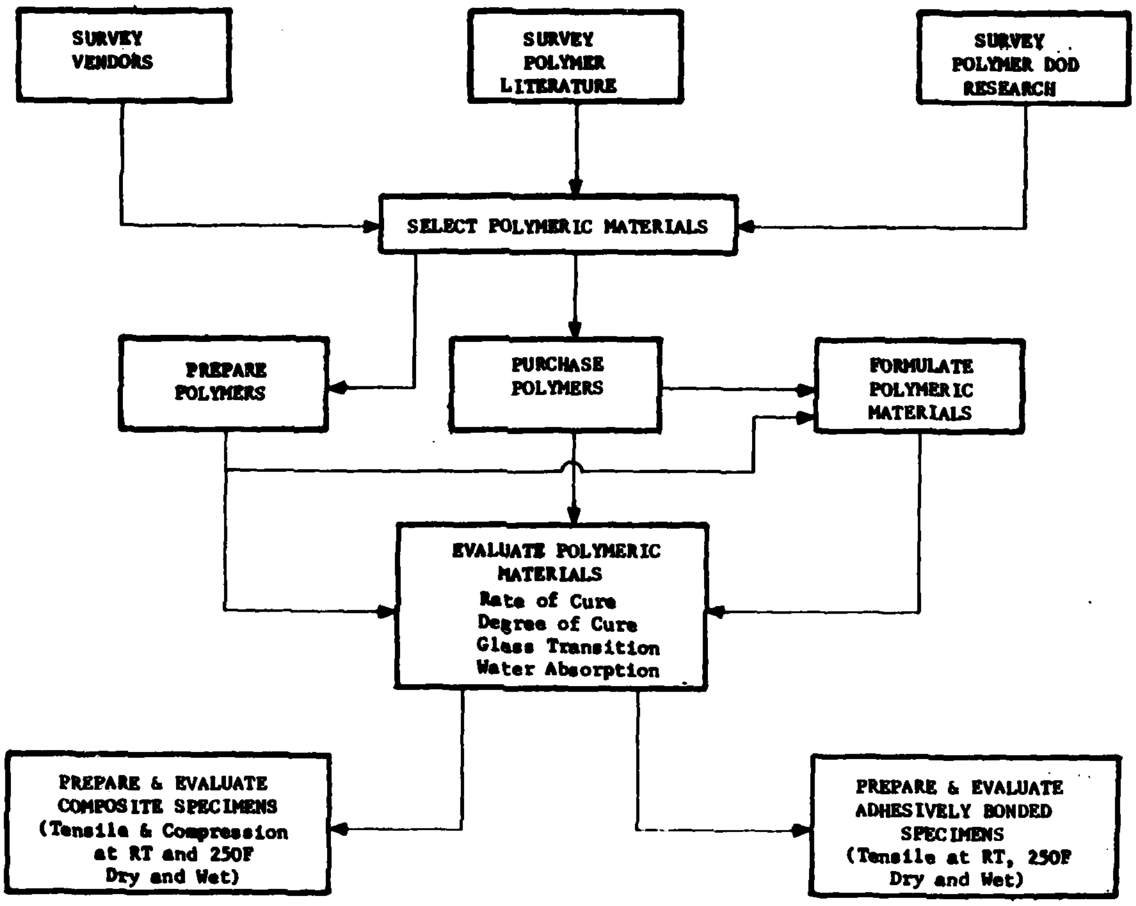


Figure 7. Program Methodology

(3) Near Infrared Analysis (NIR). NIR was used to monitor the rate at which reactive molecular species such as vinyl and epoxide groups disappear during cure.

(4) Dynamic Mechanical Analysis (DMA). DMA was used to measure shear modulus, effect of temperature on modulus, glass transition temperature, and low temperature polymer transitions (measure of polymer toughness).

2.4 ELEVATED TEMPERATURE TESTING

Special mention needs to be made of the way in which elevated mechanical properties were determined. Two methods of testing were considered. In the first method, elevated temperature properties were determined by heating the test specimens to test temperature rapidly and applying load as soon as they reached test temperature. There was no thermal "soak" before applying the load. This minimized postcuring and generated data which were true measures of the thermal stability of ambient cured polymers. In the second method, the specimens were loaded to design stress at room temperature and then heated to 121C (250F) at the rate at which the aircraft heats during flight. This simulates the worst possible case: an aircraft flown on a "hot" day in which it reaches 99C (210F) shortly after having been repaired. The polymer is postcured during this heatup which is beneficial; however, it may creep as it is heated under load. This method of testing measured the competing effects of postcure and creep. The majority of the data presented in this report were generated using the first method of testing. Since the skin temperature of an aircraft is reported to be heated at rates of 50-100F/minute, these rapid heat-up rates were used.

2.5 EVALUATION OF ADHESIVES BY LAP SHEAR STRENGTH TESTING

Formulated and commercial adhesives were evaluated by preparing and testing lap shear tensile coupons. Both aluminum/aluminum and graphite/epoxy coupons were used. These tests were selected as an inexpensive rapid screening method for the adhesives to determine the capability of the adhesives to carry mechanical loads and to measure how much strength retention each adhesive has at 121C (250F). Peel loads are introduced in this type of lap shear test so no adhesive would be eliminated from further evaluation in this program based

solely upon these tests. The aluminum coupons were used in these tests because aluminum surface treated by the phosphoric acid anodize (BAC 5555) method gives us a bonding surface of known high quality and this eliminates any uncertainty about the surface in evaluating an adhesive. Details of the preparation of the lap shear coupons are presented in Table 3.

TABLE 3. LAP SHEAR TEST SPECIMEN PREPARATION

	Graphite/Epoxy Coupons	Aluminum Coupons
Material	AS/3501-6	7075-T6
Coupon Size	5.00 x 0.50 inch	5.00 x 1.00 inch
Overlap	0.50 inch	0.50 inch
Surface Preparation	Sanding with #100 Emery paper, MEK solvent wipe	Phosphoric acid anodize (BAC 5555)
Cure Pressure	Spring clamps	Deadweight load (contact pressure)
Cure Time and Temperature	48 hours @ RT	48 hours @ RT
Bondline Thickness	Approximately 0.001 inch	Approximately 0.003 inch

2.6 UTILIZATION OF REPAIR MATERIALS

There are several material forms in which the polymer systems may be used to repair damaged graphite/epoxy composite structures. These are summarized in Table 4.

2.7 EPOXY RESIN FORMULATIONS

Epoxy resins were given a thorough evaluation in the program because they offer such an outstanding combination of mechanical and adhesive properties. Fourteen epoxy resins and twelve curing agents were evaluated in this program. Listings of the resins and curing agents used are given in Tables 5 and 6. Forty-five formulations of these resins and curing agents were evaluated. An initial screening of the formulations was made by DSC analysis. The formulations were evaluated by heating them in a scanning DSC analysis at 10C/minute to determine the temperature at which exotherm occurs.

Table 4. Material Forms for Patches

Material Form	Method of Application	Advantages	Disadvantages
1. Precured graphite/epoxy patch (e.g. AS/3501-6 with 0/±45/90 ply orientation protected by peel ply.	Remove peel ply. Cover laminate patch with film or paste adhesive. Clamp or hold in place with vacuum until cured.	Excellent for flat surfaces. Incorporates high strength laminate into the repair structure.	Not applicable to contoured surfaces.
2. Precured graphite/epoxy patch (e.g. AS/3501-6 with 0/±45/90 ply orientation covered with ambient temperature or low temperature curing film or paste adhesive that is protected by polyethylene film.	Remove protective film from adhesive. Activate the surface of the adhesive with the appropriate activator. Clamp or hold in place with vacuum until cured.	Same as above. In addition, the adhesive will not have to be applied separately.	Not applicable to contoured surfaces. Anaerobic curing adhesives will require special packaging to prevent cure in storage.
3. Dry woven graphite fabric coated with ambient temperature or low temperature curing liquid resin.	Prepare a wet layup over the damaged surface area. Use film or paste adhesive or resin bonds.	Simple operation. Uses well-established boat repair technology. Useful for both flat and contoured adhesive.	Cured laminate will almost certainly have a high resin content and a low fiber volume.
4. Low temperature curing graphite prepreg tape or fabric.	Position uncured prepreg over damaged surface using film or paste adhesive. Apply heat as required. Use vacuum bag pressure during cure.	Useful for both flat and contoured surfaces.	The mechanical strength using vacuum bag cured laminates will be less than that from the autoclave cure of the AS/3501-6 precured patches.

The peak exotherm temperature determined by differential scanning calorimetry of each resin system are listed in Table 7. Those resin systems which have peak cure exotherms at 100C or show exotherm behavior in the temperature range 90-120C were found to be acceptable systems for cure in the ambient temperature range required for this program.

The best resin systems were those that contained high molecular weight, high functionality resins such as ECN 1299 and/or low molecular weight liquid resins such as 0510 or MY-720. These formulations had significantly improved load carrying capability at 121C (250F) compared to formulations of the Epon 828/DETA type.

TABLE 5. EPOXY RESINS USED

EPOXY RESIN (TRADE NAME)	SUPPLIER	CHEMICAL STRUCTURE	EPOXIDE EQUIVALENT WEIGHT
0510	Ciba-Geigy	Triglycidyl ether of p-amino phenol	100
MY-720	Ciba-Geigy	Tetraglycidyl ether of 4,4'-methylene dianiline	120
DER 332	Dow	Diglycidyl ether of bisphenol A	172 - 176
Epon 828	Shell	Diglycidyl ether of bisphenol A	185 - 192
Epon 836	Shell	Diglycidyl ether of bisphenol A	290 - 335
Epon 1001	Shell	Diglycidyl ether of bisphenol A	450 - 550
Epon 1004	Shell	Diglycidyl ether of bisphenol A	895 - 1025
Epon 1007	Shell	Diglycidyl ether of bisphenol A	2000 - 2500
Epon 1009	Shell	Diglycidyl ether of bisphenol A	2500 - 4000
Epon 1031	Shell	Polyglycidyl ether of tetraphenylene ethane	210 - 240
ECN 1235	Ciba-Geigy	Polyglycidyl ether of orthocresol-formaldehyde novolac	215
ECN 1299	Ciba-Geigy	Polyglycidyl ether of orthocresol-formaldehyde novolac	225
SU-8	Celanese	Epoxy novalac	210
Apogen 101	Shaefer Chemicals	Diglycidyl ether of bisphenol A containing two methylol groups per bisphenol A	205 - 225
Epon 871	Shell	Flexibilized epoxy	200

TABLE 6. CURING AGENTS USED FOR EPOXY RESINS

Trade Name	Supplier	Chemical Structure
DETA	Dow	Polyamine (diethylene triamine)
AEP	Shell	Aminoethyl piperazine
T-403	Jefferson Chemical Co.	Trifunctional primary aliphatic amine
V-40	Shell	Polyamide
HAP-22*	Jefferson Chemical Co.	Mixture of polymethylene cyclohexylamine isomers
PACM-20	duPont	Cycloaliphatic diamine
Epon D	Shell	Polyamine salt
Epon T-1	Shell	Polyamine
398	Jefferson Chemical Co.	Polyamine
DMP-10	Ciba-Geigy	Phenol
DMP-30	Ciba-Geigy	Phenol
1-methyl imidazole	Aldrich	Imidazole

*No longer commercialy available.

TABLE 7. EPOXY FORMULATIONS EVALUATED

Formulation	Peak DSC Exotherm Temperature, °C
Apogen 101/HAP-22 (5/1.25)	95
DER 332/HAP-22 (5/1.50	125
DER 332/T-403 (5/1.90)	140
0510/AEP (5/2.15)	Exotherm @ 90
0510/HAP-22/398 (10/5.25/1.0)	110
0510/HAP-22 (5/2.62)	125
Apogen 101/HAP-22/398 (5/1.25/0.52)	95
Apogen 101/0510/HAP-22/398 (5/5/3.54/1.0)	100
0510/HAP-22/AEP (5/1.95/0.5)	120
0510/T-403 (5/3.35)	135
MY-720/T-403 (5/2.8)	150
MY-720/HAP-22 (5/2.2)	135
Apogen 101/0510/HAP-22/AEP (5/5/2.90/2.36)	100
0510/HAP-22/1-methylimidazole (5/1.97/0.10)	Exotherm @ 130
0510/Apogen 101/HAP-22/ 1-methylimidazole (5/5/3.85/0.20)	125
0510/HAP-22/1-methylimidazole/398 (5/1.94/0.19/0.12)	125
DER 332/1-methylimidazole (5/0.1)	154
DER 332/T-1 (5/1.30)	90
0510/T-1 (5/2.30)	85
DER 332/Epon D (5/0.50)	125
0510/1-methylimidazole (5/0.10)	160
0510/Apogen 101/HAP-22 (5/5/3.88)	115
Epon 828/0510/DETA (5/5/1.60)	100

TABLE 7. EPOXY FORMULATIONS EVALUATED (Continued)

Formulation	Peak DSC Exotherm Temperature, °C
DER 332/PACM-20 (5/1.50)	120
Apogen 101/0510/PACM-20/AEP (5/5/2.91/2.32)	100
0510/PACM-20/398 (5/2.70/0.53)	110
Epon 828/DMP-10 (5/0.5)	115
Epon 828/DMP-30 (10/1)	109
Apogen 101/0510/PACM-20 (2/2/1.55)	110
Epon 828/T-403	125
0510/PACM-20/DMP-10 (5/2.64/0.07)	125
DER 332/DMP-10 (5/0.26)	125
Epon 858/PACM-20 (5/1.42)	123
Epon 1001/0510/PACM-20/DMP-30 (5/5/3.62/0.1)	120
0510/PACM-20 (5/2.63)	125
Epon 828/DETA (10/1.1)	105
ECN 1299/MY-720/0510/AEP (5/5/5/4.86)	115
ECN 1299/0510/AEP (5/5/3.0)	Exotherm @ 90
ENC 1299/0510/AEP/1-methylimidazole (5/5/3.06/0.08)	98
Epon 1001/0510/PACM-20 (5/5/3.15)	120
ECN 1299/0510/DETA/DMP-30	110
ECN 1299/0510/PACM-20 (5/5/3.74)	125
ECN 1299/0510/DETA (5/5/1.5)	Exotherm @ 95
0510/DETA (5/1.05)	Exotherm @ 100
SU-8/0510/DETA (5/5/1.55)	99

In these systems the solid high functionality resins were dissolved in the liquid epoxy resins. By employing the liquid epoxy as a "solvent" it was practical to use solid, high functionality resins for 24C (75F) cures. The resin system which was most extensively investigated was formulated with ECN 1299, 0510, and DETA curing agent.

2.7.1 The ECN 1299/0510/DETA Epoxy Formulation

This formulation was prepared with ECN 1299, a solid (melting point approximately 110C) epoxy cresol novalac manufactured by Ciba-Geigy, 0510 a very low viscosity trifunctional epoxy also made by Ciba-Geigy, and DETA (diethylene triamine) liquid epoxy curing agent. The mixture was prepared in the following ratio: 5 parts ECN-1299, 5 parts 0510, and 1.5 parts DETA. The 0510 served as a solvent for the solid ECN-1299. The mixture of the two resins was heated to approximately 350F and stirred to obtain a well-mixed solution. At room temperature the mixture was a viscous paste which could be mixed with the DETA. The ECN-1299/0510 mixture without DETA can be stored for long periods of time and therefore is a practical system for field repair.

This epoxy formulation gave excellent lap shear strength results. The formulation cured 24 hours at 24C (75F) on aluminum had lap shear strengths in the following ranges: (1) at -55C (-67F): 1960 to 3140 psi; (2) at 24C (75F): 3070 to 4040 psi; (3) at 82C (180F): 2170 to 4190 psi; at 105C (220F): 1850 to 2760 psi; and at 121C (250F): 1280 to 1780 psi. These results are tabulated in Tables 8 and 9.

TABLE 8. ECN-1299/0510/DETA EPOXY LAP SHEAR TENSILE STRENGTH,
ALUMINUM COUPONS* - 24C (75F) CURE FOR 72 HOURS
TEST TEMPERATURES: -67F, 75F, AND 180F

Coupon No.	Lap Shear Strength @ -55C (-67F), psi	Lap Shear Strength @ 24C (75F), psi	**Lap Shear Strength @ 82C (180F), psi
1	2760	3500	4190
2	3140	3070	2810
3	2540	4040	2170
4	1960	3870	3870
Average	2600	3620	3260

* Coupons described in Table 3.

** Rapid heat up to test temperature; immediate application of load.

TABLE 9. ECN 1299/0510/DETA EPOXY LAP SHEAR TENSILE STRENGTH, ALUMINUM COUPONS*
24C (75F) CURE FOR 72 HOURS
TEST TEMPERATURES: 104C (220F) AND 121C (250F)***

Coupon No.	** Lap Shear Strength @ 105C (220F), psi	** Lap Shear Strength @ 121C (250F)
1	2760	1710
2	2360	1720
3	1850	1780
4	2320	1740
5	2420	1280
6	2080	1300
7	2250	1310
8	2150	1310
9		1280
10		1320
11		1410
12		1300
13		1400
14		1270
15		1180
16		1520
Average	2280	1430

* Coupons described in Table 3.

** Rapid heat up to test temperature; immediate application of load.

The most likely reason for the success of this system is that it consists of a high chain stiffness polymer (ECN-1299) dissolved in a matrix epoxy (0510) which is highly reactive and cures to a high crosslink density. The high chain stiffness epoxy gives good thermal stability while the highly reactive matrix gives fast cure times. The curing agent (DETA) is highly reactive in the temperature range 10C to 38C (50F to 100F).

An evaluation was made to determine why such high lap shear results at elevated temperatures are obtained from this resin system after only an ambient temperature cure. A sample of the resin was heated in a differential scanning calorimetric (DSC) cell from room temperature to 121C (250F) at 50C/minute and held at temperature for two minutes. The DSC cell was used for this because it gives very accurate heat up rates and temperature control. The 50C/minute was used as the heat up rate because aircraft skins are often heated at this rate during flight. A sample of resin "cured" in the DSC was then evaluated by thermomechanical analysis (TMA). The TMA evaluation is shown in Figure 8. It shows that no softening occurs in the resin as it is heated to 180C (356F) indicating that the resin cures extremely rapidly during the 50C/minute heat up and two minute hold at 121C (250F).

In addition, a dynamic mechanical analysis was made of the ambient temperature cured system as it was heated from -120C (-184F) to 180C (356F) at 5C/min. This analysis (Figure 9) shows that the resin begins to enter a rubbery state at 75C but it cures rapidly at the same time. It cures so rapidly that it quickly passes into a glassy rigid state and remains a rigid material as it is heated up to 180C.

Since good results were obtained with the ECN 1299/0510 resin mixture, other mixtures of solid and liquid epoxies were evaluated. The following solid resins were used: Epon 1031 (Shell); SU-8 (Celanese); ECN 1235 (Ciba-Geigy); Epon 1001, 1004, 1007 and 1009 (Shell). Epon 1031, SU-8, and ECN 1235 are all high functionality resins which should give good high temperature performance. The Epon 1001 through 1009 series are low functionality, high molecular weight resins which should give fast cures and good toughness.

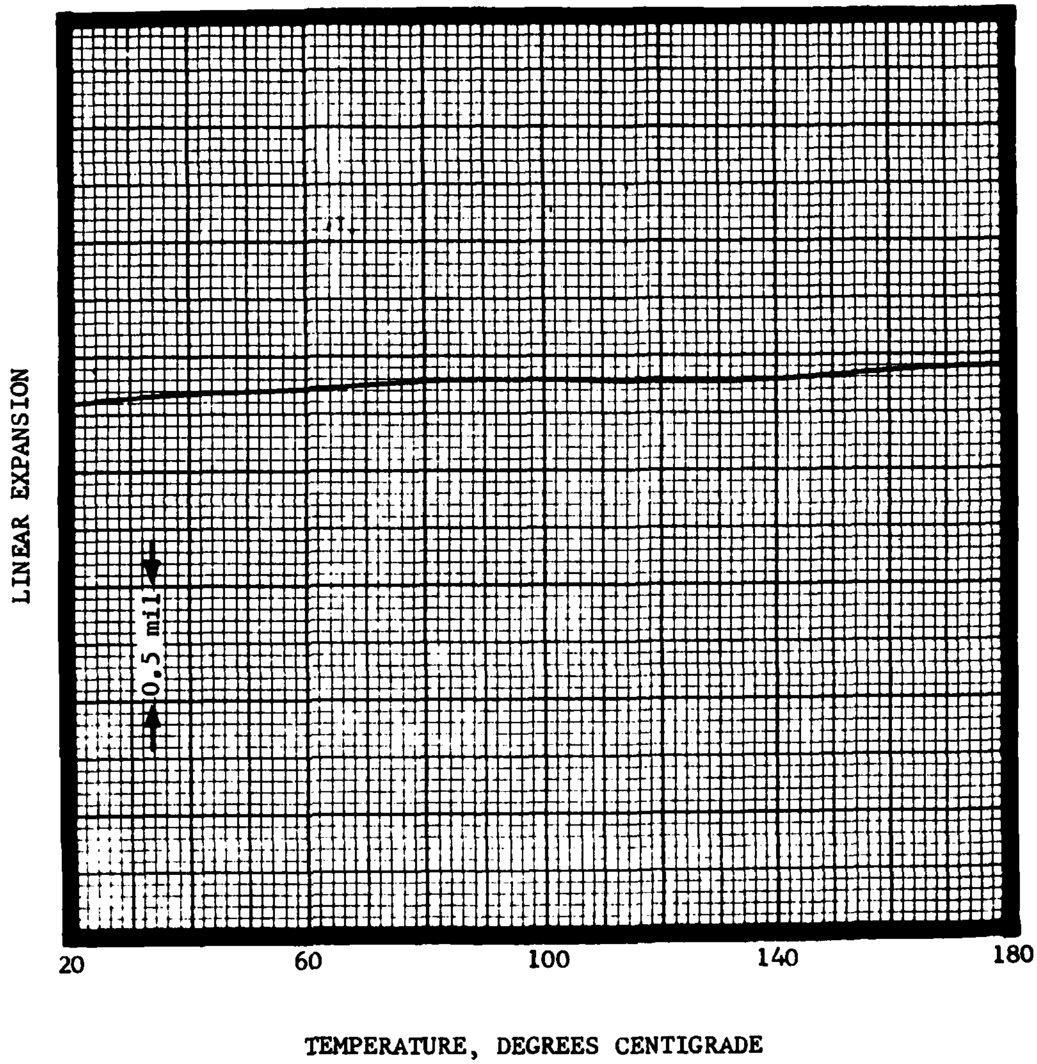


Figure 8. Thermal Mechanical Analysis of 1299/0510/DETA After 24 Hours Cure @ 24C (75F), Heat Up to 121C (250F) at 50C/Minute and 2 Minute Hold at 121C (250F)

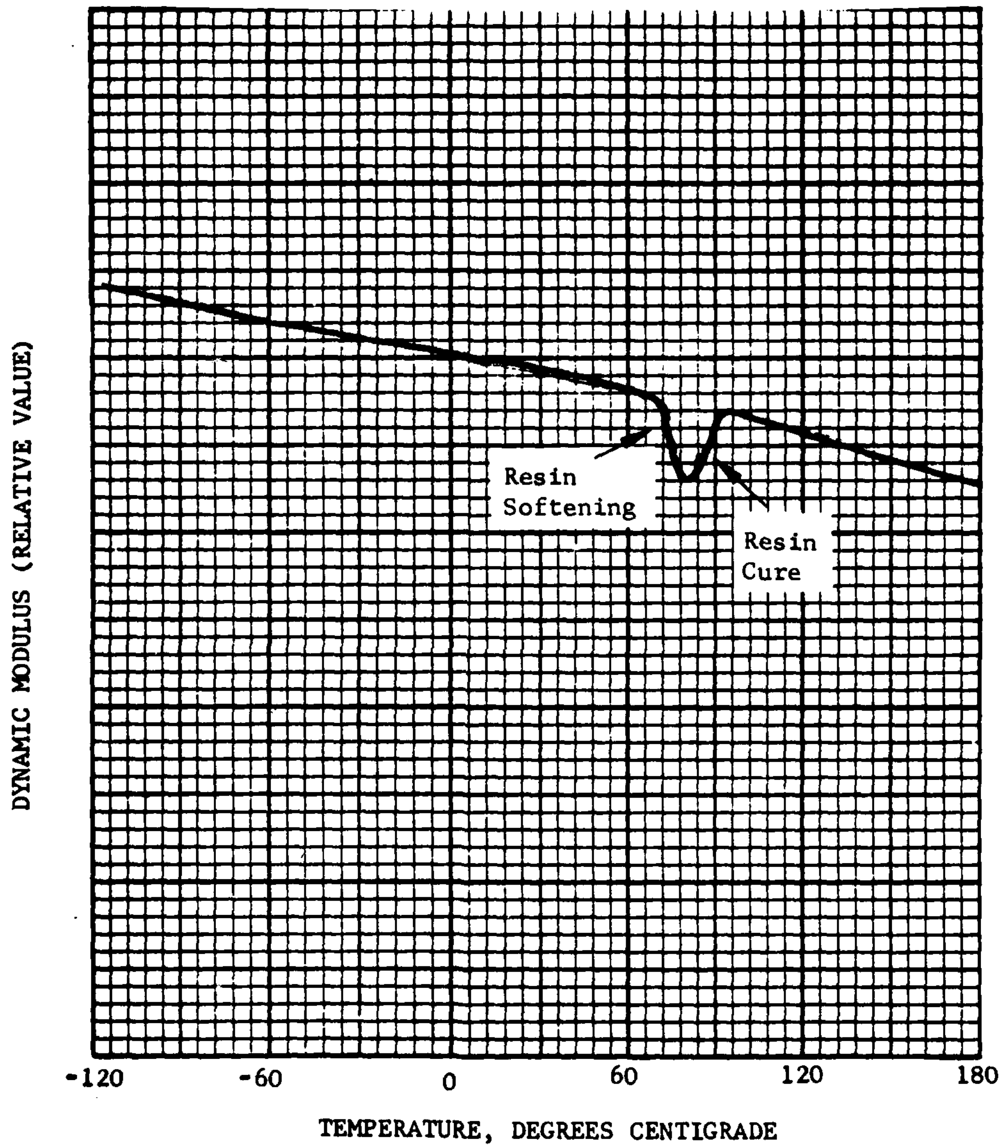


Figure 9. Dynamic Mechanical Analysis of ECN 1299/0510/DETA

Four liquid resins were used: MY-720 (Ciba-Geigy), Epon 828 (Shell), Epon 871 (Shell), and Apogen 101 (Schaeffer). MY-720 is a tetrafunctional resin which should give excellent high temperature performance. Epon 828 is a good general purpose, low cost epoxy. Epon 871 is a toughening agent. Apogen 101 is a very rapid curing resin. The following curing agents were used: DETA, PACM-20, and V-40.

The formulations evaluated are listed in Table 10. The test results are summarized in Table 11. Some of the formulations gave very encouraging results in the testing at 121C (250F). For example, Apogen 101/0510/DETA, SU-8/0510/DETA, Epon 1031/0510/DETA, and ECN 1235/0510/DETA all showed good lap shear strength at 121C (250F). Average strengths were as high as 1500 psi. Individual coupons had strengths as high as 1900 psi. It shows this type of formulation is very versatile and numerous resins can be used to tailor properties to a specific objective.

TABLE 10. 24C (75F) TEMPERATURE CURING EPOXY FORMULATIONS EVALUATED

Formulation	Composition
Epon 828/0510/DETA	(10/10/3.24)
Epon 828/MY-720/DETA	(10/10/3.24)
Epon 1001/0510/DETA	(8/10/2.42)
Epon 1004/0510/DETA	(8/15/2.28)
Epon 1007/0510/DETA	(8/15/2.17)
Epon 1009/0510/DETA	(10/21/4.46)
ECN 1299/0510/V-40	(10/10/5)
ECN 1299/0510/V-40	(10/10/12)
ECN 1299/MY-720/0510/DETA	(8/10/8/4.14)
ECN 1299/Epon 828/DETA	(10/16/1.99)
ECN 1235/0510/DETA	(10/10/3.05)
Apogen 101/0510/DETA	(15/15/4.65)
ECN 1299/0510/PACM-20	(10/10/7.54)
Epon 1031/0510/DETA	(10/10/3.05)
SU-8/0510/DETA	(10/10/3.10)
ECN 1299/Epon 871/0510/DETA	(10/10/5/3.00)

TABLE 11. EPOXY ADHESIVES, LAP SHEAR TENSILE STRENGTH, ALUMINUM COUPONS*
24C (75F) CURE FOR 72 HOURS
TEST TEMPERATURE: 24C (75F) AND 121C (250F)

Adhesive	Coupon No.	Lap Shear Strength @ 24C (75F), psi	** Lap Shear Strength @ 121C (250F)
ECN 1299/ Epon 828/DETA	1	3670	620
	2	3130	490
	3	3350	700
	4	3190	890
	Average	3340	650
SU-8/0510/ DETA	1	2370	1370
	2	2360	1450
	3	2130	1420
	4	2360	1350
	Average	2300	1400
Epon 1031/ 0510/DETA	1	1990	1250
	2	2300	1300
	3	2510	1300
	4	2230	1410
	Average	2260	1320
Epon 1001/ 0510/DETA	1	1590	1010
	2	1820	1350
	3	1510	1100
	4	1090	1110
	Average	1500	1140
Epon 1004/ 0510/DETA	1	1040	620
	2	1070	820
	3	1040	1410
	4	1220	910
	Average	1100	940

* Coupons described in Table 3.

** Rapid heat up to test temperature; immediate application of load.

TABLE 11. EPOXY ADHESIVES, LAP SHEAR TENSILE STRENGTH, ALUMINUM COUPONS*
24C (75F) CURE FOR 72 HOURS
TEST TEMPERATURE: 24C (75F) AND 121C (250F)
(Continued)

Adhesive	Coupon No.	Lap Shear Strength @ 24C (75F), psi	** Lap Shear Strength @ 121C (250F)
Epon 1007/ 0510/DETA	1	1060	530
	2	1040	380
	3	760	1010
	4	940	330
	Average	950	560
Epon 1009/ 0510/DETA	1	1820	1300
	2	1920	1290
	3	1990	1070
	4	2210	1230
	Average	1990	1220
ECN 1235/ 0510/DETA	1	1650	1520
	2	1780	1560
	3	1690	1400
	4	1730	1750
	Average	1710	1560
Apogen 101/ 0510/DETA	1	2370	1920
	2	2400	1750
	3	2430	830
	4	--	1740
	Average	2400	1560
ECN 1299/ 0510/V-40 (10/10/5)	1	1960	70
	2	1870	110
	3	1930	70
	4	1890	90
	Average	1910	85

* Coupons described in Table 3.

** Rapid heat up to test temperature; immediate application of load.

TABLE 11. EPOXY ADHESIVES, LAP SHEAR TENSILE STRENGTH, ALUMINUM COUPONS*
24C (75F) CURE FOR 72 HOURS
TEST TEMPERATURE: 24C (75F) AND 121C (250F)
(Continued)

Adhesive	Coupon No.	Lap Shear Strength @ 24C (75F), psi	** Lap Shear Strength @ 121C (250F)
Epon 828/ MY-720/DETA	1	2420	1860
	2	2180	1520
	3	2260	1640
	4		1260
	Average	2290	1570
Epon 828/ 0510/DETA	1	2600	--
	2	2900	--
	3	2570	--
	4	2980	--
	Average	2760	--
ECN 1299/ 0510/PACM-20	1	--	970
	2	--	1300
	3	--	1310
	4	--	1210
	Average	--	1200
ECN 1299/ Epon 871/ 0510/DETA	1	2610	1250
	2	3120	990
	3	3690	1070
	4	3210	990
	Average	3160	1080

* Coupons described in Table 3.

** Rapid heat up to test temperature; immediate application of load.

The high molecular weight, high functionality resin systems also look promising as adhesives that cure rapidly at moderate temperatures. Figures 10 through 15 show the rate at which the epoxide groups react at temperatures in the range 60C (140F) to 100C (212F) for various epoxy formulations. These analyses were made by near infrared spectroscopy at 2200 nanometers. Cure is complete when the absorbance at 2200 nanometers becomes zero.

The ECN 1299/0510/DETA formulation cured rapidly at temperatures 75C (167F), 100C (212F), and 121C (250F). The glass transition temperature of the ECN 1299/0510/DETA formulation cured 30 minutes at temperatures in the range 75C (167F) to 177C (350F) was determined by TMA. Results are listed in Table 12. The glass transition temperature increased from 104C (219F) for the 75C (167F) cure to 150C (302F) for the 177C (350F) cure.

The rapid cure of this formulation at moderate temperature was verified by lap shear testing. Aluminum/aluminum lap shear panels were cured 24 hours at 24C (75F) and then postcured one hour at 67C (150F) or 93C (200F). The lap shear tensile strengths obtained at 121C (250F) on these specimens are shown in Table 13.

Lap shear strengths in the range 2200 to 2750 psi were obtained at 121C (250F) after the postcure at 93C (200F).

2.7.2 Creep Testing of 24C (75F) Cured Adhesives

Tests were made to determine how much creep occurs in ambient temperature cured adhesive bonds which are heated to 105C (220F). In these tests the bonds were placed under load at room temperature, 24C (75F), and heated to 105C (220F) at 50F/minute. The elongation of the bond during the heat up was monitored. For the ECN 1299/0510/DETA system cured at 24C (75F) aluminum/aluminum bonds loaded at 400 psi or less showed no creep whatever in these tests. A specimen loaded at 600 psi began to creep at 75C (167F).

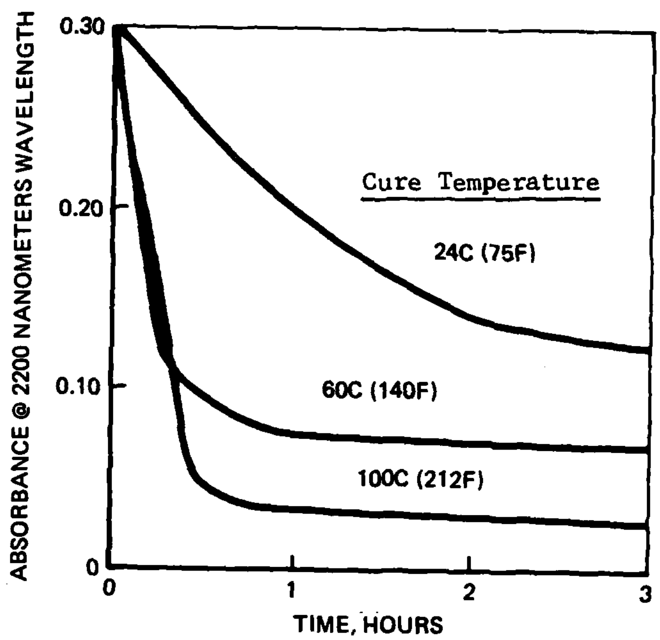


Figure 10. Rate of Cure Analysis of ECN 1299/0510/DETA Formulation Made Using Near Infrared Analysis

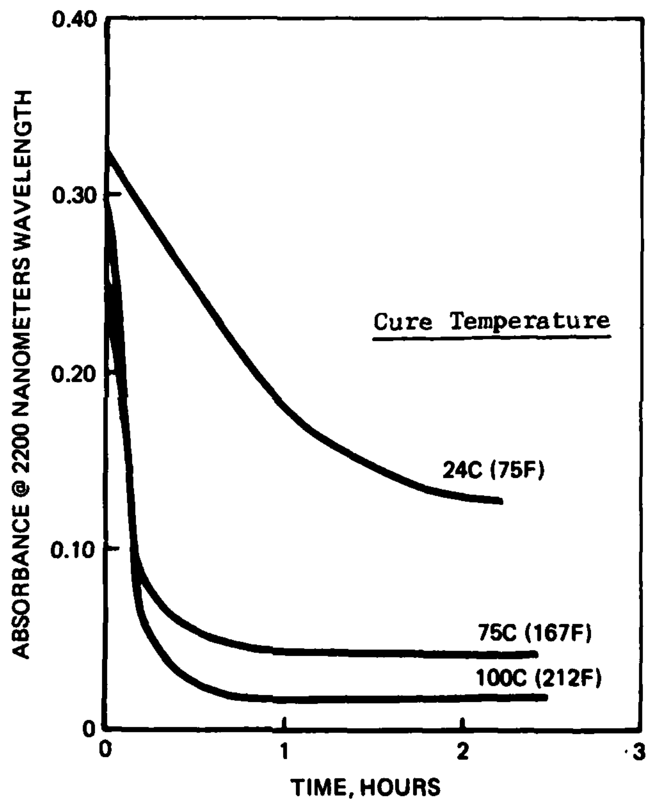


Figure 11. Rate of Cure Analysis of Epon 1001/0510/DETA Formulation Made Using Near Infrared Analysis

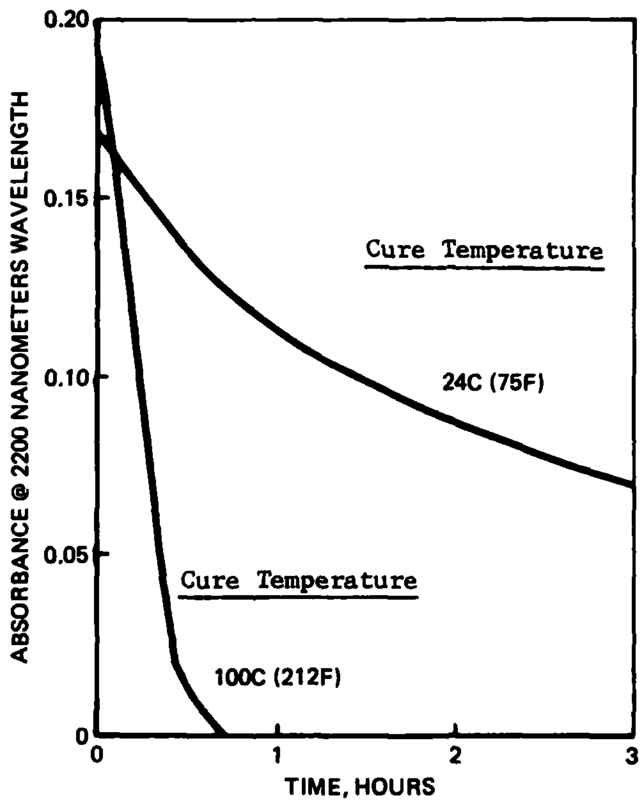


Figure 12. Rate of Cure Analysis of Epon 1004/0510/AEP Formulation Made Using Near Infrared Analysis

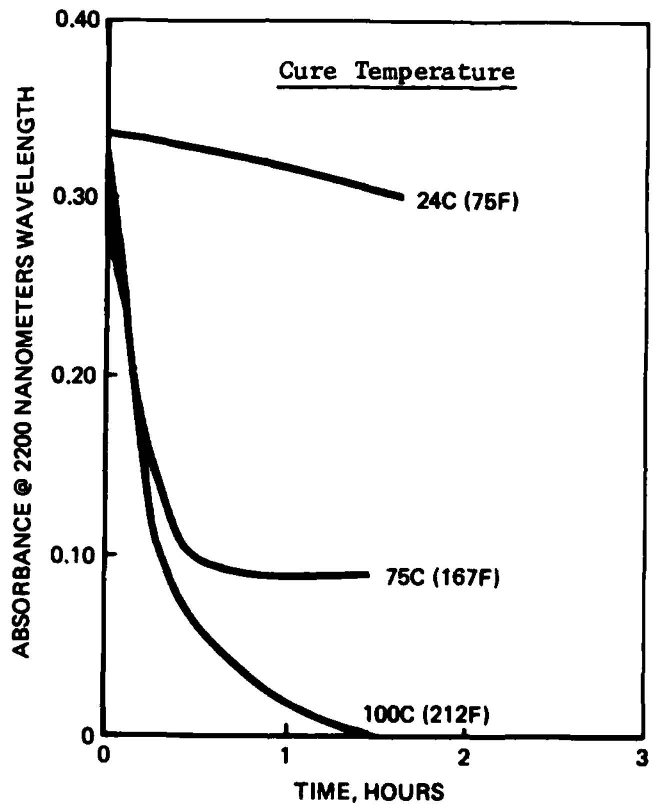


Figure 13. Rate of Cure Analysis of 0510/PACM-20 Formulation Made Using Near Infrared Analysis

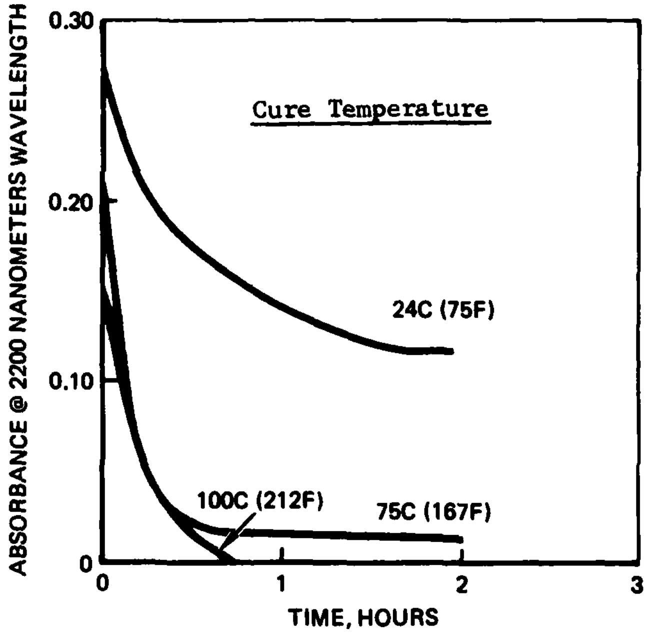


Figure 14. Rate of Cure Analysis of Apogen 101/PACM-20 Formulation Made Using Near Infrared Analysis

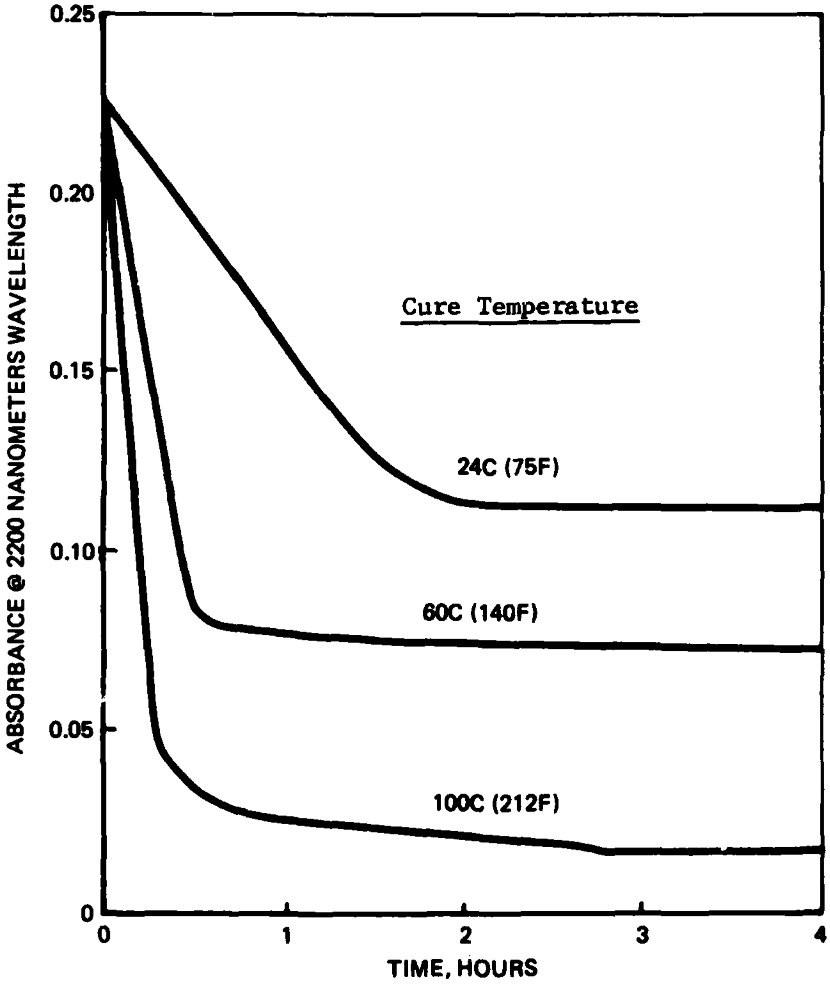


Figure 15. Rate of Cure Analysis of SU-8/0510/DETA Formulation Made Using Near Infrared Analysis

TABLE 12. GLASS TRANSITION TEMPERATURE OF ECN 1299/0510/DETA CURED AT ELEVATED TEMPERATURES

Cure Temperature	Cure Time, Minutes	Glass Transition Temperature*
75C (167F)	30	104C (219F)
100C (212F)	30	128C (262F)
121C (250F)	30	147C (297F)
177C (350F)	30	150C (302F)

* Determined by TMA using a 10 psi load and using a 5C/minute heat up rate.

TABLE 13. ECN-1299/0510/DETA EPOXY ADHESIVE LAP SHEAR TENSILE STRENGTH ALUMINUM COUPONS*

CURED: 24C (75F) FOR 72 HOURS WITH POSTCURE AT 150F OR 200F FOR 1 HOUR

Postcure Temperature	Coupon No.	* Lap Shear Strength @ 121C (250F)
150F	1	1840
	2	1620
	3	1950
	4	1930
	Average	1840
200F	1	2750
	2	2200
	3	2280
	4	2640
	Average	2470

* 10 minute soak at 121C (250F) before testing

2.7.3 Water Absorption Measurements

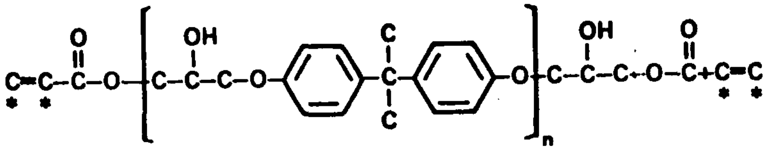
In order to gain some measurement of environmental durability of the epoxy formulations, resin samples were immersed in deionized water at 82C (180F) until the weight gain reached a constant level. The equilibrium weight gains of various formulations are shown in Table 14. The weight gain of Hercules 3501-6 epoxy resin formulation is included in the table for comparison because it is used extensively on the F-18A aircraft. Some of the resins show greater water absorption and some showed less water absorption than 3501-6. It may be possible to significantly lower the water absorption by replacing DETA with another curing agent. Replacing DETA with PACM-20, for example, reduced the water absorption of the ECN 1299/0510 formulation from 9.0% to 4.2%.

TABLE 14. WATER ABSORPTION OF EPOXY ADHESIVE FORMULATIONS
WEIGHT GAIN AT EQUILIBRIUM IN 82C (180F) DEIONIZED WATER

Formulation	Equilibrium Weight Gain, Wt. %
3501-6 (Hercules)	6.50
ECN 1299/0510/PACM-20	4.20
Epon 1031/0510/DETA	8.50
ECN 1299/Epon 828/DETA	2.90
ECN 1299/0510/DETA	9.00
SU-8/0510/DETA	9.30
Epon 1001/0510/DETA	6.10
Epon 1007/0510/DETA	6.70
Epon 1009/0510/DETA	9.80

2.8 Vinyl Ester Resins

Vinyl ester resins contain terminal carbon-carbon unsaturation and therefore can be cured by peroxides, such as methyl ethyl ketone peroxide (MEKP), cumene hydroperoxide (CHP), and benzoyl peroxide (BPO), which are activated at room temperature by amines and cobalt napthenate (CoNap). Figure 16 shows the chemical structure of the vinyl ester resin.



n = 1 or 2

*denotes reactive sites, terminal carbon-carbon unsaturation

Figure 16. Chemical Structure of Vinyl Ester Resin

Due to their structure, vinyl ester resins are reported to have improved toughness, environmental durability, and adhesive properties compared to other carbon-carbon unsaturated resins such as the isopthalic polyesters and the bisphenol A-fumaric acid polyesters. The vinyl ester resin is either self-curing or can be cured with mono, di, or polyfunctional crosslinkers. Dow markets these resins under the Derakane trade name. They come in a variety of formulations. Generally they contain styrene as a crosslinker. For high temperature applications Derakane 470-36 is the most promising of the Derakanes which contain styrene. Dow sells the pure vinyl ester resin as Derakane XD9002. Styrene is not the best crosslinker because it presents potential health hazards, it is very volatile, and being monofunctional, polymer structures cured with it have limited thermal stability. Di and polyfunctional crosslinkers have greater potential.

2.8.1 Styrene Crosslinked Vinyl Ester Resins

MEKP Catalyzed Formulations. The glass transition temperature of Derakane 470-36 formulations were as high as 130C (266F) when cured in masses as small as 10 grams at an ambient temperature of 24C (75F) with MEKP, dimethyl aniline (DMA), and cobalt napthenate (CoNap).

Several Derakane 470-36 formulations were evaluated. These formulations are shown in Table 15. The formulations are shown with the glass transition temperatures obtained with an ambient temperature cure of 24 hours at 24C (75F). High glass transition temperatures are obtained when high exotherm temperatures are developed.

TABLE 15. GLASS TRANSITION TEMPERATURES OF DERAKANE 470-36 FORMULATIONS CURED AT 24C (75F)

Formulation	Weight in Grams				Glass Transition Temp. T_g
	Derakane 470-36	MEKP	CoNap	DMA	
1	10.0	0.10	0.03	0.03	130C (266F)
2	10.0	0.10	0.04	0	25C (77C)
3	10.0	0.10	0.01	0.03	130C (266F)
4	10.0	0.10	0.01	0	50C (122F)
5	10.0	0.20	0.07	0	95C (203F)

The vinyl ester resin catalyzed with MEKP is a high exotherm system. In the 10 gram masses the exotherm reached 300F in formulation #1, 225 in formulation #5 during an ambient temperature cure at 24C (75F). The exotherms versus time after initial mixing for these formulations are shown in Figure 17. Formulations #2 and #4 did not have exotherms large enough to be measured. Test samples were machined out of these castings and were analyzed by DSC and TMA. DSC showed that formulations #1, #3, and #5 were fully cured while #2 and #4 were not. Formulations #1 and #3 both had glass transition temperatures of 130C (266F). The glass transition temperatures of #2 and #4 were much lower as shown in Table 15. A thermomechanical analysis of formulation #1 from which the glass transition temperature measurement was obtained is shown in Figure 18. Five formulations of 470-36 catalyzed with MEPK were exposed to moisture to determine their equilibrium level of water absorption. Samples were immersed in 180F deionized water for approximately 60 days. 180F was used rather than room temperature to accelerate the testing.

The amount of water absorbed at equilibrium was low compared to the water absorbed by 3501-6 epoxy. The 470-36 formulations absorbed only 1 to 2% water. Results are shown in Table 16. Under the same conditions 3501-6 absorbs 6 to 7%. The absorption versus time curves for two of the five

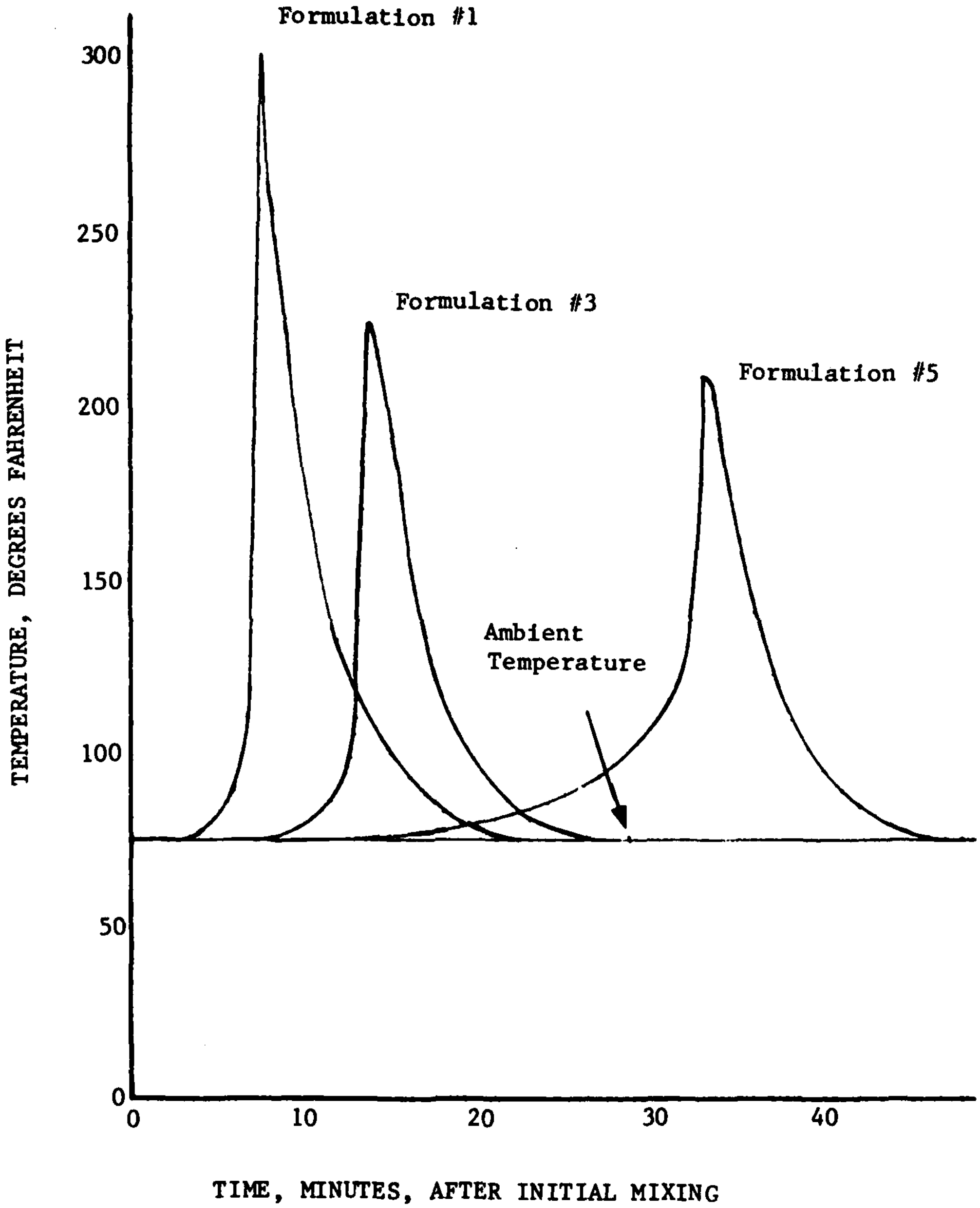


Figure 17. Exotherms for Various Vinyl Ester Formulations (See Table 15 for Composition of the Formulations)

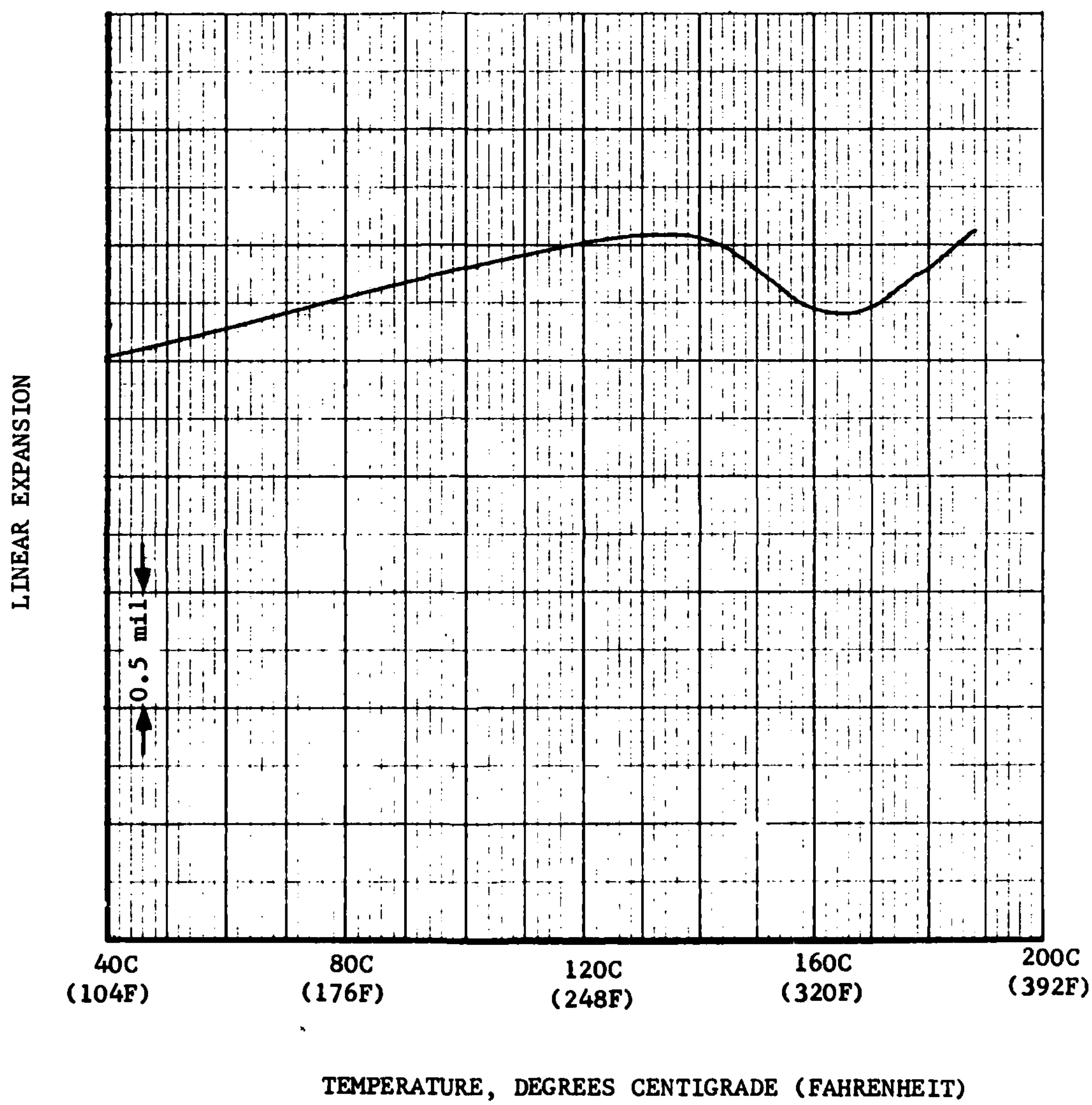


Figure 18. Thermal Mechanical Analysis of Vinyl Ester Resin Formulation #1 (See Table 15) - Cure 2 Hours @ 24C (75F)

formulations are shown in Figure 19. The curves for the other three formulations are similar. The absorption curves are typical of what is obtained with nonhydrolyzable resins. The weight gain reaches a constant level. Hydrolyzable resins show a peak water absorption followed by rapid weight loss as the hydrolyzed compounds are dissolved by the water. The water absorption results are encouraging since they show the vinyl ester resins absorb only one-sixth the water 3501-6 absorbs at equilibrium.

Aluminum/aluminum lap shear panels were bonded at 24C (75F) using the 470-36 470-36 formulation #1 (see Table 15). The panels were prepared using the procedure outlined in Table 3 and tested at room temperature and at 121C (250F). Results are tabulated in Table 17. Room temperature tensile strength is in the range 1400 to 1900 psi. Tensile strength at 121C (250F) was in the range 200 to 600 psi. The results were low at high temperature because in the thin film without the aluminum/aluminum panels the resin did not reach a high enough exotherm temperature to achieve a high level of cure. The main application for MEKP catalyzed vinyl ester resin appears to be as a moderate temperature curing adhesive.

TABLE 16. EQUILIBRIUM WATER ABSORPTION AT 180F OF VINYL ESTER (DERAKANE 470-36) FORMULATIONS

Formulation	Formulation: Weight in Grams				Equilibrium Water Absorption, wt, %
	Derakane 470-36	MEKP	CoNap	DMA	
1	10.0	0.10	0.03	0.03	1.2
2	10.0	0.10	0.04	0	1.6
3	10.0	0.10	0.01	0.03	1.1
4	10.0	0.10	0.01	0	1.5
5	10.0	0.20	0.07	0	1.0

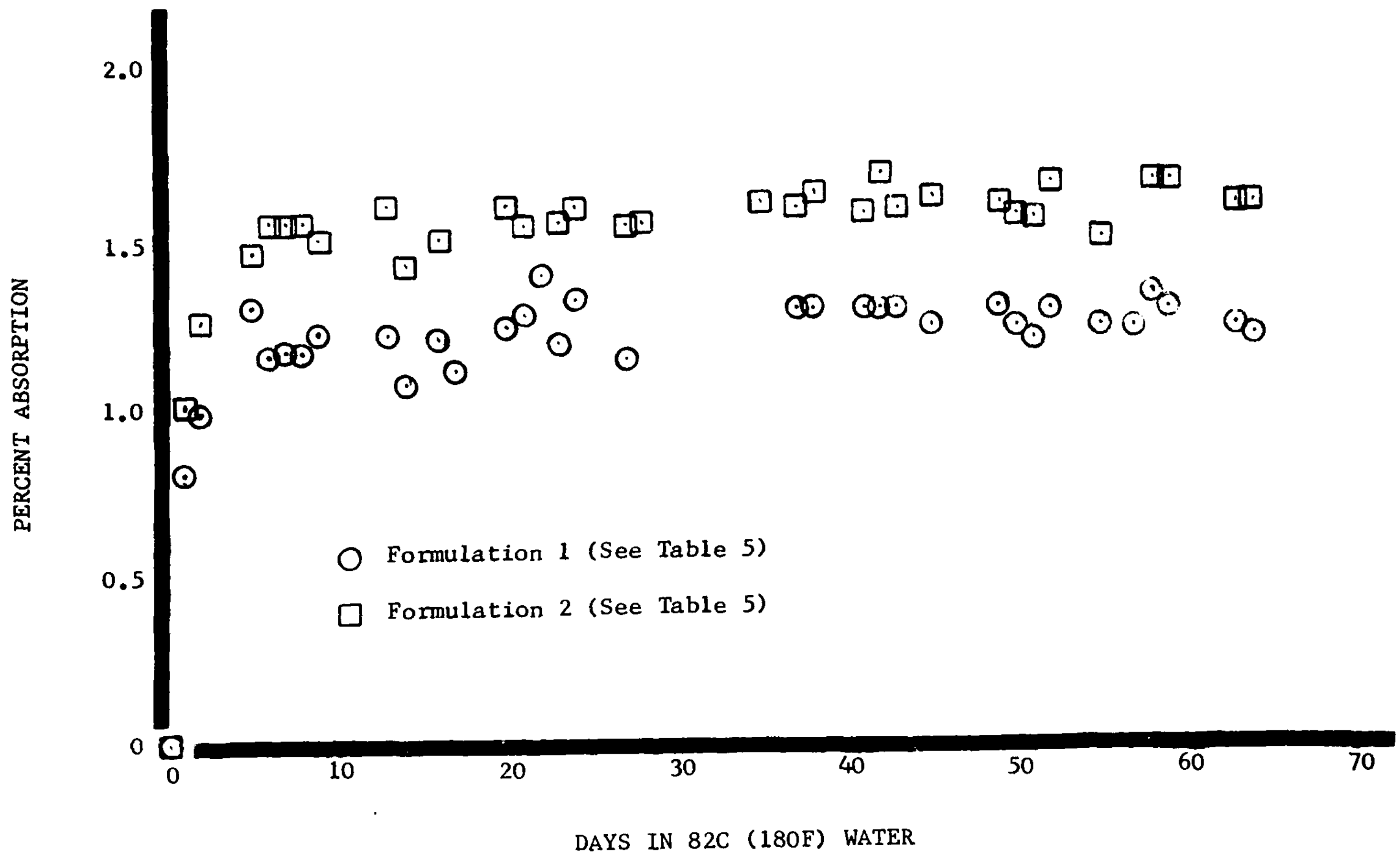


Figure 19. Water Absorption Versus Time For Vinyl Ester Formulation

TABLE 17. VINYL ESTER (DERAKANE 470-36) LAP SHEAR TENSILE STRENGTH
ALUMINUM COUPONS*
Cure: 72 Hours at 24C (75F)

Adhesive	Coupon No.	Lap Shear Strength @ 24C (75F), psi	** Lap Shear Strength @ 121C (75F)
Formulation #1 (See Table 15)	1	1440	220
	2	1640	380
	3	1870	150
	4	1760	590
	Average	1680	340

*Coupons described in Table 3.
** Rapid heat up to test temperature; immediate application of load.

2.8.2 Cumene Hydroperoxide (CHP) Catalyzed 470-36

Formulations of 470-36/CHP were catalyzed with various mixtures of cobalt napthenate (CoNap), dimethylaniline (DMA), and CHP. The formulations evaluated are listed in Table 18. The formulations were mixed and cured at 24C (75F) for 48 hours. None of the formulations, in 10 gram masses, showed an exotherm of more than a few degrees.

Thermal mechanical analyses (TMA) were made on these resins to determine their softening temperatures. The highest softening temperatures were approximately 60C (140F). A typical TMA analysis is shown in Figure 20.

CHP catalyzed vinyl ester resins cannot be used for ambient temperature cure. They may find application as moderate temperature curing adhesives.

2.8.3 Vinyl Ester Resins with Compounds Other Than Styrene

There are many reactive crosslinkers which can be used to react with vinyl ester resins in place of styrene. The objective is to use crosslinkers which will give resins with controlled properties such as crosslink density, toughness, and elongation. Numerous crosslinkers are available from the Sartomer Company. These are listed in Table 19. A thorough evaluation of these crosslinkers needs to be made.

TABLE 18. DERAKANE 470-36/CUMENE HYDROPEROXIDE FORMULATIONS

Formulation	Derakane	CHP	CoNAP	DMA
6	50	1.00	0.10	0.10
7	50	1.00	0.10	0.05
8	50	1.00	0.05	0.05
9	50	1.00	1.10	0
10	50	0.75	0.10	0
11	50	1.00	0	0
12	50	0.75	0.10	0
13	50	0.50	0.10	0
14	50	0.50	0.05	0

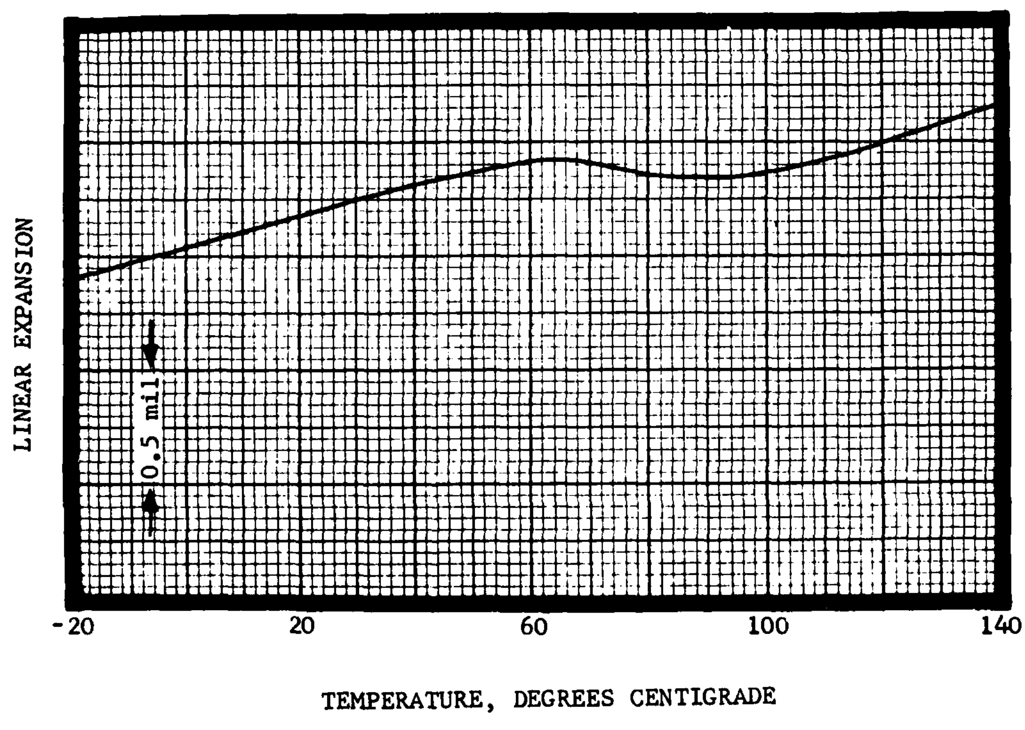
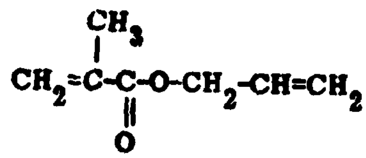


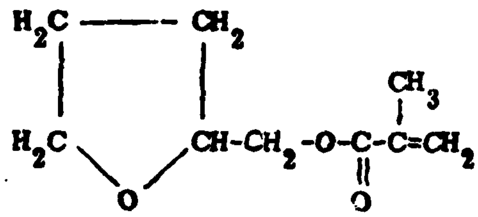
Figure 20. Thermal Mechanical Analysis of Vinyl Ester Resin Formulation #7 (See Table 18) Cured 48 Hours @ 24C (75F)

TABLE 19. SARTOMER CROSSLINKERS

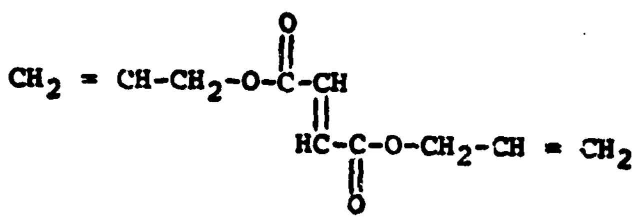
ALLYL
METHACRYLATE



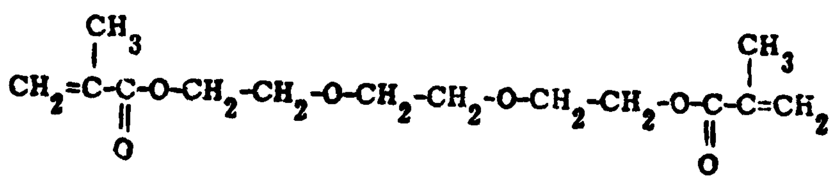
TETRAHYDROFUR-
FURYL METHACRYLATE



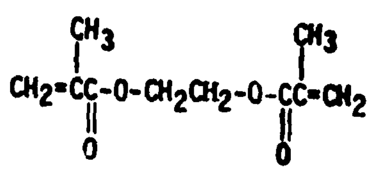
DIALLYL FUMARATE



TRIETHYLENE
GLYCOL
DIMETHACRYLATE



ETHYLENE GLYCOL
DIMETHACRYLATE



CYCLOHEXYL
METHACRYLATE

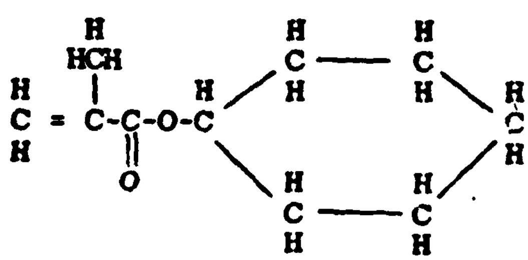


TABLE 19. SARTOMER CROSSLINKERS (Continued)

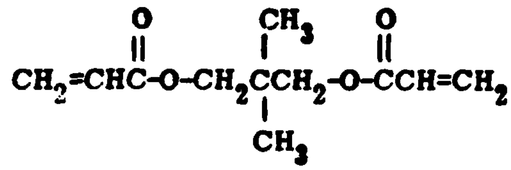
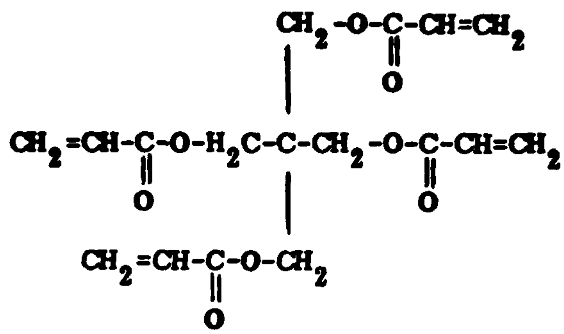
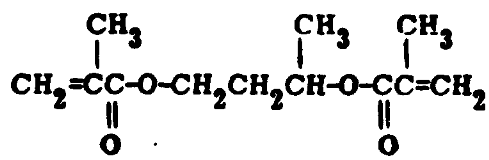
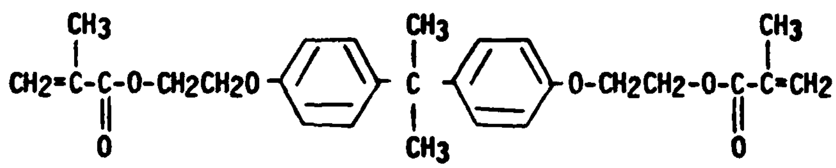
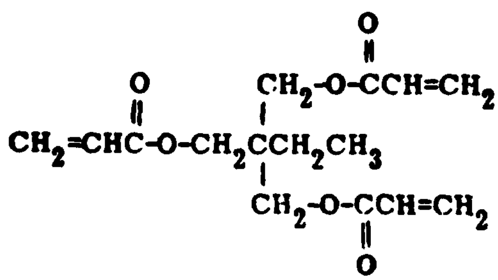
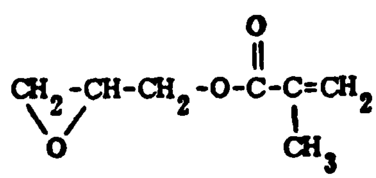
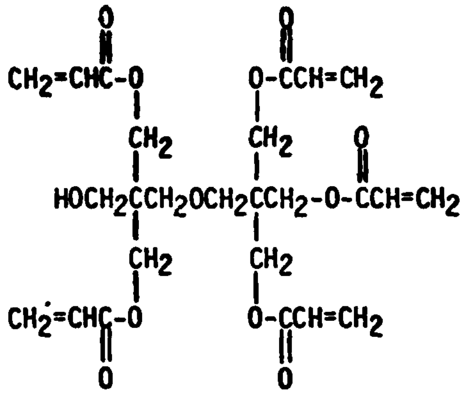
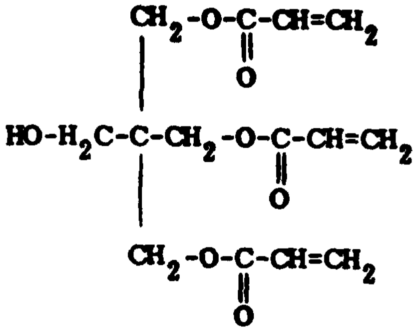
NEOPENTYL GLYCOL DIACRYLATE	
PENTAERYTHRITOL TETRAACRYLATE	
1,3-BUTYLENE GLYCOL DIMETHACRYLATE	
ETHOXYLATED BISPHENOL-A DIMETHACRYLATE	
TRIMETHYLOL PROPANE TRIACRYLATE	
GLYCIDYL METHACRYLATE	

TABLE 19. SARTOMER CROSSLINKERS (Continued)

DIPENTAERYTHRITOL MONOHYDROXYPENTA ACRYLATE



PENTAERYTHRITOL TRIACRYLATE



2.9 ANAEROBIC ADHESIVES

Anaerobic adhesives were evaluated because it is well established that they cure rapidly at room temperatures. The chemical structure of a typical anaerobic curing polymer is shown in Figure 21. The unsaturated chain terminating sites cure by addition reactions that are inhibited in the presence of air. As soon as the air is removed, cure proceeds rapidly.

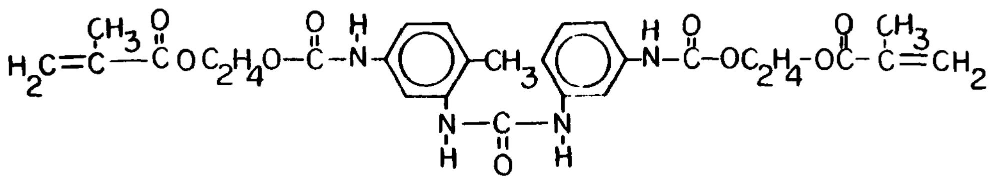


Figure 21. Chemical Structure of Typical Anaerobic Polymer

The test results on anaerobic adhesives that were evaluated are listed in Tables 20 and 21. Some of these adhesives were reported to have service temperatures as high as 275 to 400F. However, in the tests conducted in this program with rapid heat up rates and no soak time at test temperature, none of the anaerobics had acceptable lap shear tensile strength at 121C (250F). At this temperature most of the lap shear tensile strengths were in the range 100-600 psi. The test results on aluminum/aluminum lap shear are presented in Table 20. The test results obtained on graphite/epoxy lap shear bonds are presented in Table 21.

Thermomechanical analyses show why these anaerobics have very poor elevated temperature performance following cure at 24C (75F). They have softening temperatures at or only slightly above the ambient temperature at which they were cured. The thermomechanical analyses of Loctite 324 and 325 are shown in Figures 22 through 25.

Most of the anaerobic adhesives had excellent handling properties and would be ideal for field repair work from a handling standpoint. They are easy to apply and develop handling strength within three minutes.

2.10 ACRYLIC ADHESIVES

The new generation of acrylic adhesives, called reactive or second generation acrylics, were evaluated because they appeared to have the potential to meet the objectives of this program. These adhesives are known to cure rapidly at room temperature, to have high shear, impact, and peel strengths, and are reported to be usable at 121C (250F) after an ambient temperature cure. Also important is the fact that these adhesives are reported to give good bonds to oil contaminated surfaces. In field repair operations, high levels of cleanliness of the bonding surfaces may not always be obtained.

The reactive acrylics which were evaluated are shown in Tables 22 and 23 along with the test results. Results obtained on aluminum/aluminum bonds are shown in Table 22; the results obtained on graphite/epoxy bonds are shown in Table 23. The results obtained on these adhesives are very similar to the results obtained with the anaerobics. Like the anaerobics the handling properties are excellent. The adhesives are easy to apply and develop handling strength within three minutes. Lap shear strengths at 24C (77F) were good (some of the test results were as high as 4400 psi); however, the lap shear test results at 121C (250F) were very low when the bonds were only given a 24C (75F) temperature cure.

TMA analyses show that these ambient temperature cured adhesives soften at or close to the ambient temperature at which they were cured. TMA results are shown in Figures 26 to 35.

TABLE 20. ANAEROBIC ADHESIVES
LAP SHEAR TENSILE STRENGTH
ALUMINUM COUPONS*

Cure: 72 Hours at 24C (75F)

Adhesive	Coupon No.	Lap Shear Strength @ 24C (75F), psi	**Lap Shear Strength @ 121C (250F)
Speedbonder 324	1	2630	280
	2	3010	320
	3	2700	300
	4	2520	290
	Average	2720	300
Speedbonder 324	1	1700	520
	2	1600	440
	3	1400	440
	4	1670	440
	Average	1590	460
Speedbonder 324	1	1980	830
	2	1420	540
	3	710	490
	4	1570	540
	Average	1420	600
Multibond 33038	1	1710	100
	2	1700	100
	3	1880	90
	4	1810	90
	Average	1780	100

*Coupons described in Table 3.
** Rapid heat up to test temperature; immediate application of load

TABLE 20. ANAEROBIC ADHESIVES
LAP SHEAR TENSILE STRENGTH, ALUMINUM COUPONS*
(Continued)
Cure: 72 Hours at 24C (75F)

Adhesive	Coupon No.	Lap Shear Strength @ 24C (75F), psi	**Lap Shear Strength @ 121C (250F)
Quickbond 610	1	2980	420
	2	2610	390
	3	2610	420
	4	2870	440
	Average	2770	420
M300 Sumi	1	260	
	2	140	
	3	220	
	4	740	
	Average	340	
H200 Sumi	1	40	Not Tested
	2	60	
	3	480	
	4	850	
	Average	360	
3M 4173	1	340	
	2	710	
	3	930	
	4	340	
	Average	580	

*Coupons described in Table 3.
** Rapid heat up to test temperature; immediate application of load

TABLE 21. ANAEROBIC ADHESIVES
LAP SHEAR TENSILE STRENGTH
GRAPHITE/EPOXY COUPONS*

Cure: 72 Hours at 24C (75F)

Adhesive	Coupon No.	Lap Shear Strength @ 24C (75F), psi	**Lap Shear Strength @ 121C (250F)
Loctite 324	1	2040	150
	2	1580	200
	3	1660	210
	4	2040	110
	Average	1830	170
Loctite 325	1	990	190
	2	980	240
	3	1180	260
	4	1130	210
	Average	1070	220
Loctite 306	1	1470	205
	2	480	170
	3	920	210
	4	700	0
	Average	890	150

*Coupons described in Table 3.

** Rapid heat up to test temperature; immediate application of load

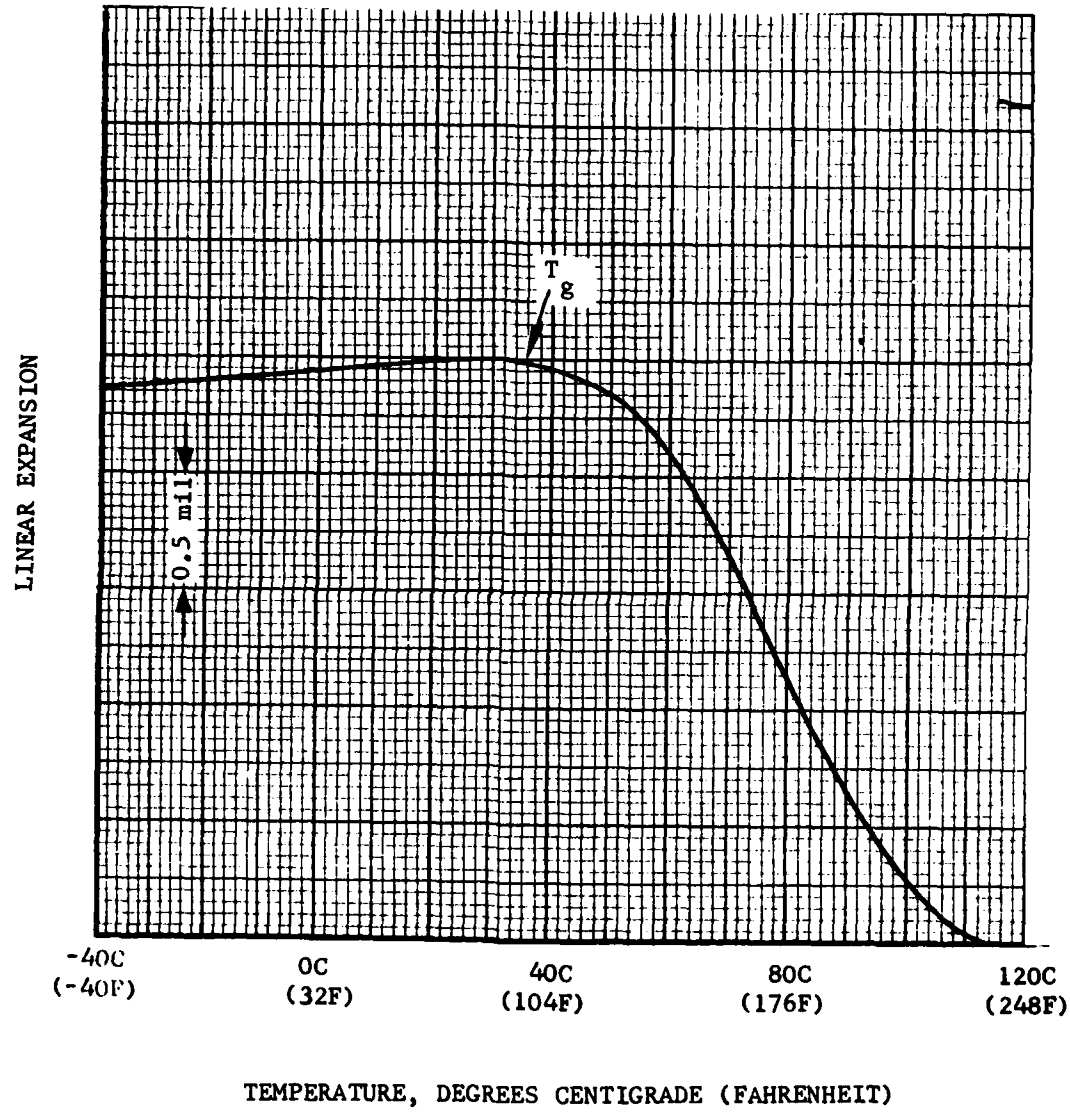


Figure 22. Thermal Mechanical Analysis of Loctite 324 Anaerobic Adhesive Cured 24 Hours @ 24C (75F)

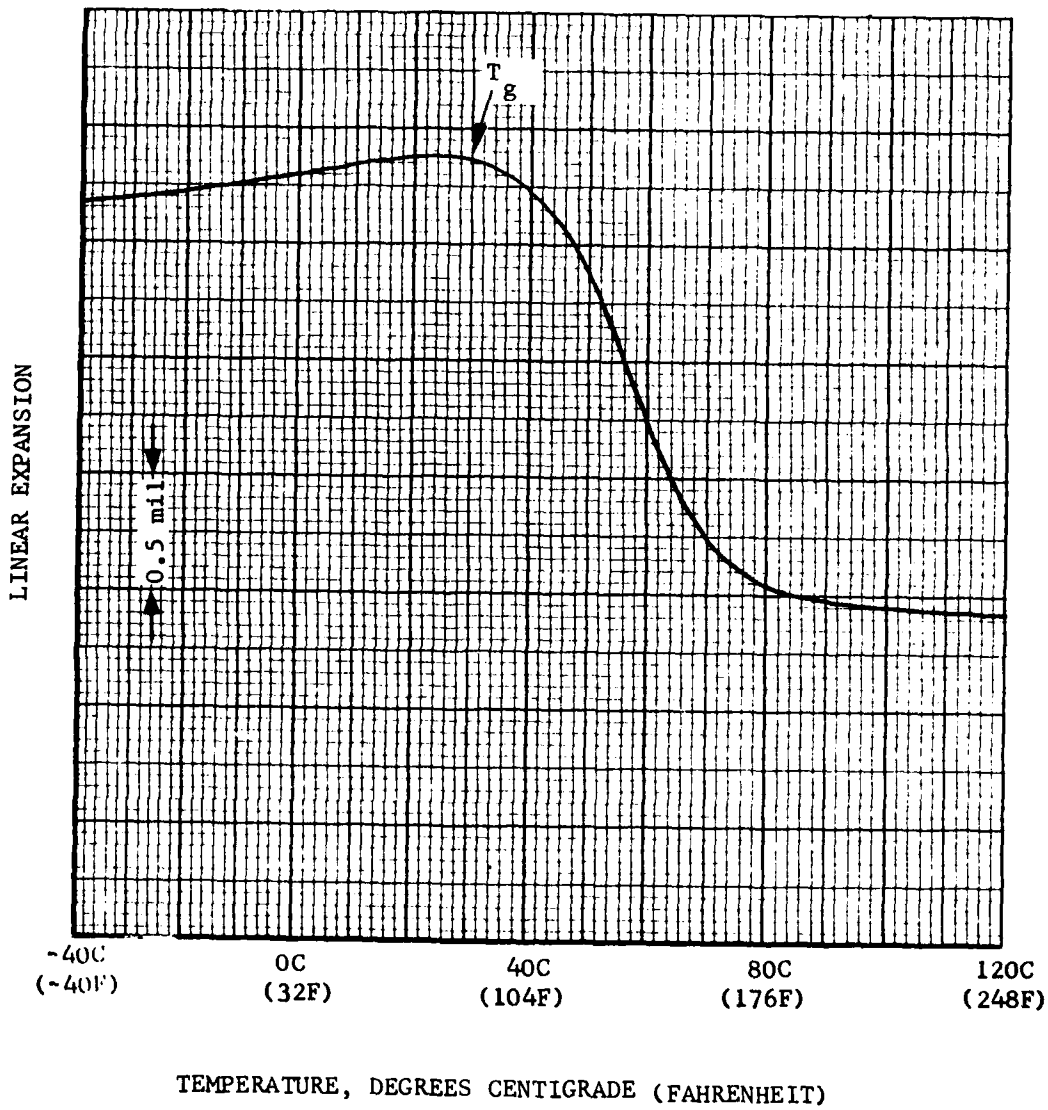


Figure 23. Thermal Mechanical Analysis of Loctite 325 Anaerobic Adhesive Cured 24 Hours @ 24C (75F)

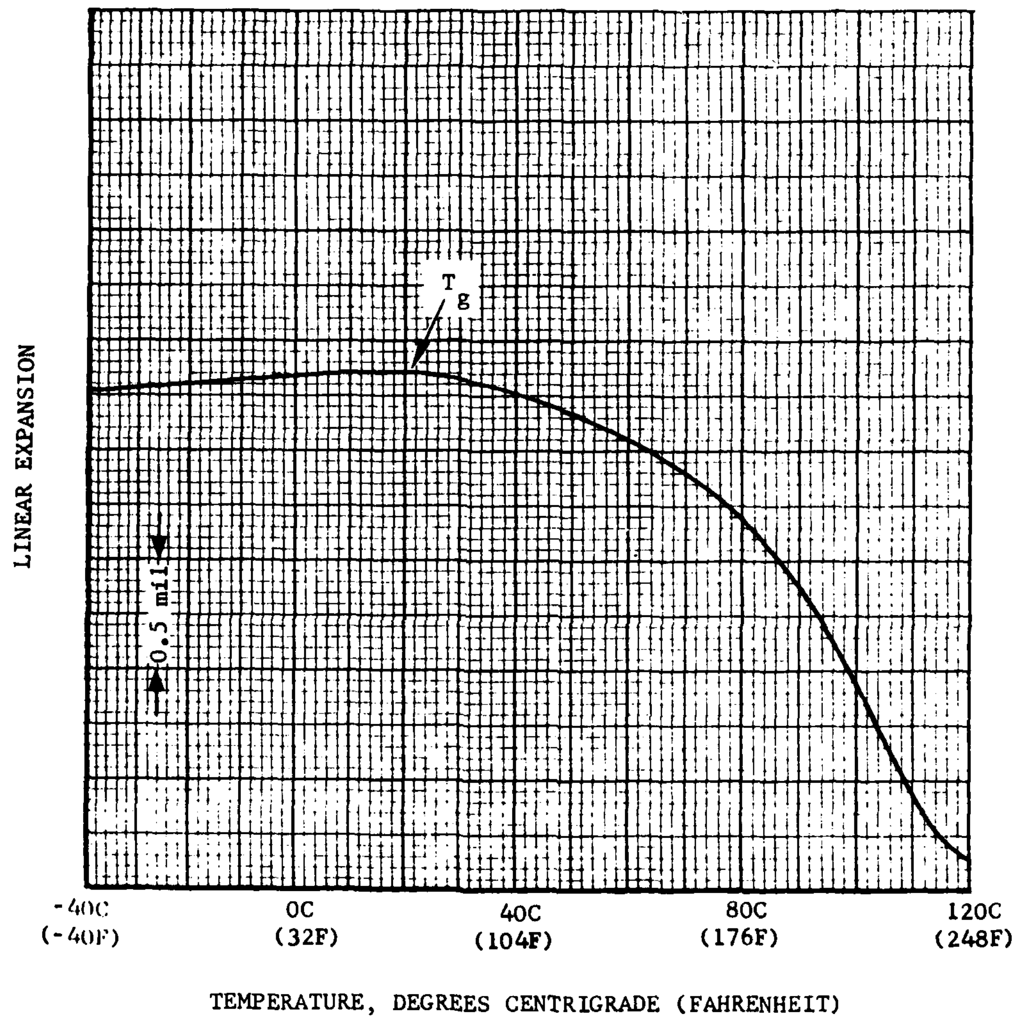


Figure 24. Thermal Mechanical Analysis of Loctite 324 Anaerobic Adhesive Cured 24 Hours @ 24C (75F) with 1 Hour Postcure @ 100C (212F)

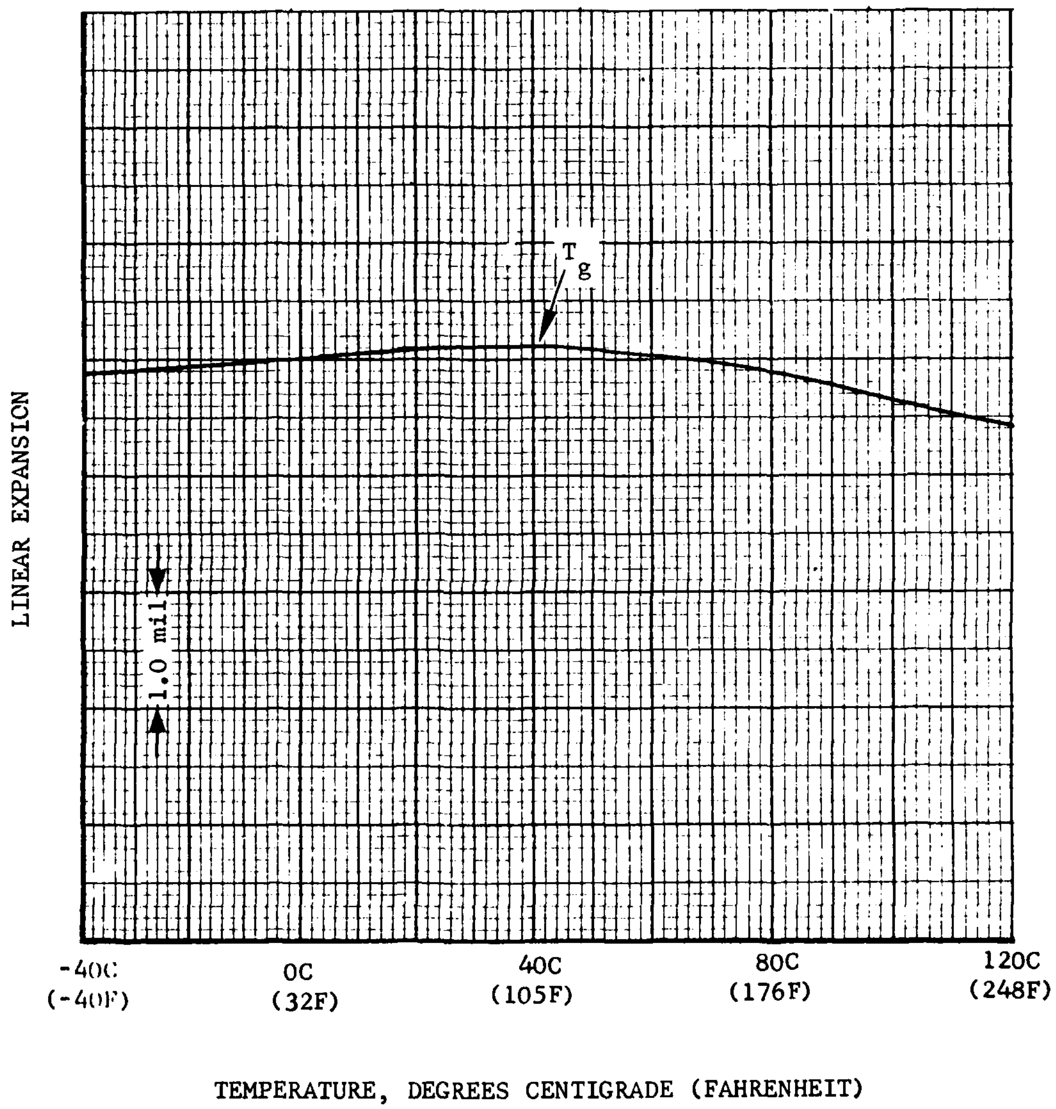


Figure 25. Thermal Mechanical Analysis of Loctite 325 Anaerobic Adhesive Cured 24 Hours @ 24C (75F) with 1 Hour Postcure @ 125C (257F)

TABLE 22. ACRYLIC ADHESIVES
LAP SHEAR TENSILE STRENGTH
ALUMINUM COUPONS*

Cure: 72 Hours at 24C (75F)

Adhesive	Coupon No.	Lap Shear Strength @ 24C (75F), psi	**Lap Shear Strength @ 121C (250F)
Weldmaster 3	1	4240	440
	2	3800	520
	3	4230	520
	4	4410	760
	Average	4170	560
Rexite IMR-P2	1	3660	550
	2	3780	780
	3	4410	930
	4	3020	800
	Average	3720	760
Versilok 513	1	3350	420
	2	1990	380
	3	2100	170
	4	2850	370
	Average	2570	340
M-890	1	3630	480
	2	3970	560
	3	3760	250
	4	3680	270
	Average	3760	390
BF-906	1	1140	370
	2	1000	370
	3	1250	340
	4	1760	370
	Average	1290	360

*Coupons described in Table 3.
** Rapid heat up to test temperature; immediate application of load

TABLE 22. ACRYLIC ADHESIVES
LAP SHEAR TENSILE STRENGTH, ALUMINUM COUPONS*
(Continued)

Cure: 72 Hours at 24C (75F)

Adhesive	Coupon No.	Lap Shear Strength @ 24C (75F), psi	**Lap Shear Strength @ 121C (250F)
ER 9446	1	1820	420
	2	1770	170
	3	2410	380
	4	2250	310
	Average	2060	320
Fuller RA-0018	1	3430	690
	2	3050	750
	3	2640	740
	4	2970	730
	Average	3020	730
BR-1177	1	2380	290
	2	2270	260
	3	2260	260
	4	2750	320
	Average	2420	280
Ren 5613	1	1490	590
	2	1890	480
	3	1340	500
	4	1660	400
	Average	1600	490

*Coupons described in Table 3.

** Rapid heat up to test temperature; immediate application of load

TABLE 23. ACRYLIC ADHESIVES
LAP SHEAR TENSILE STRENGTH
GRAPHITE/EPOXY COUPONS*

Cure: 72 Hours at 24C (75F)

Adhesive	Coupon No.	Lap Shear Strength @ 24C (75F), psi	**Lap Shear Strength @ 121C (250F)
Weldmaster 3	1	2170	440
	2	2750	420
	3	2920	260
	4	2270	910
	Average	2530	510
Rexite IMR-P2	1	1450	170
	2	1160	280
	3	1670	330
	4	1030	260
	Average	1330	260
Versilok 513	1	2120	140
	2	2310	160
	3	2030	260
	4	2750	250
	Average	2300	200

*Coupons described in Table 3.

** Rapid heat up to test temperature; immediate application of load.

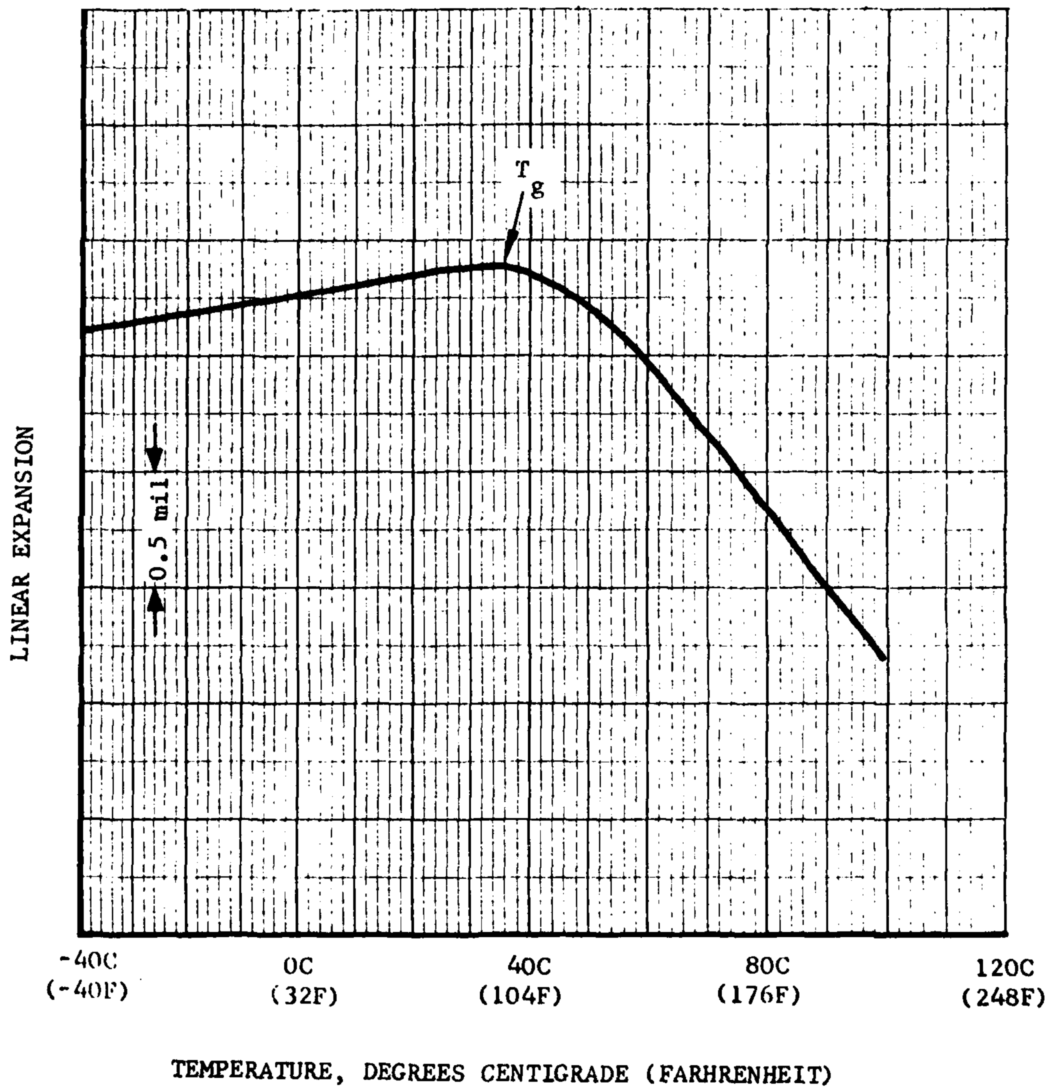


Figure 26. Thermal Mechanical Analysis of Weldmaster 3 Acrylic Adhesive
Cured 24 Hours @ 24C (75F)

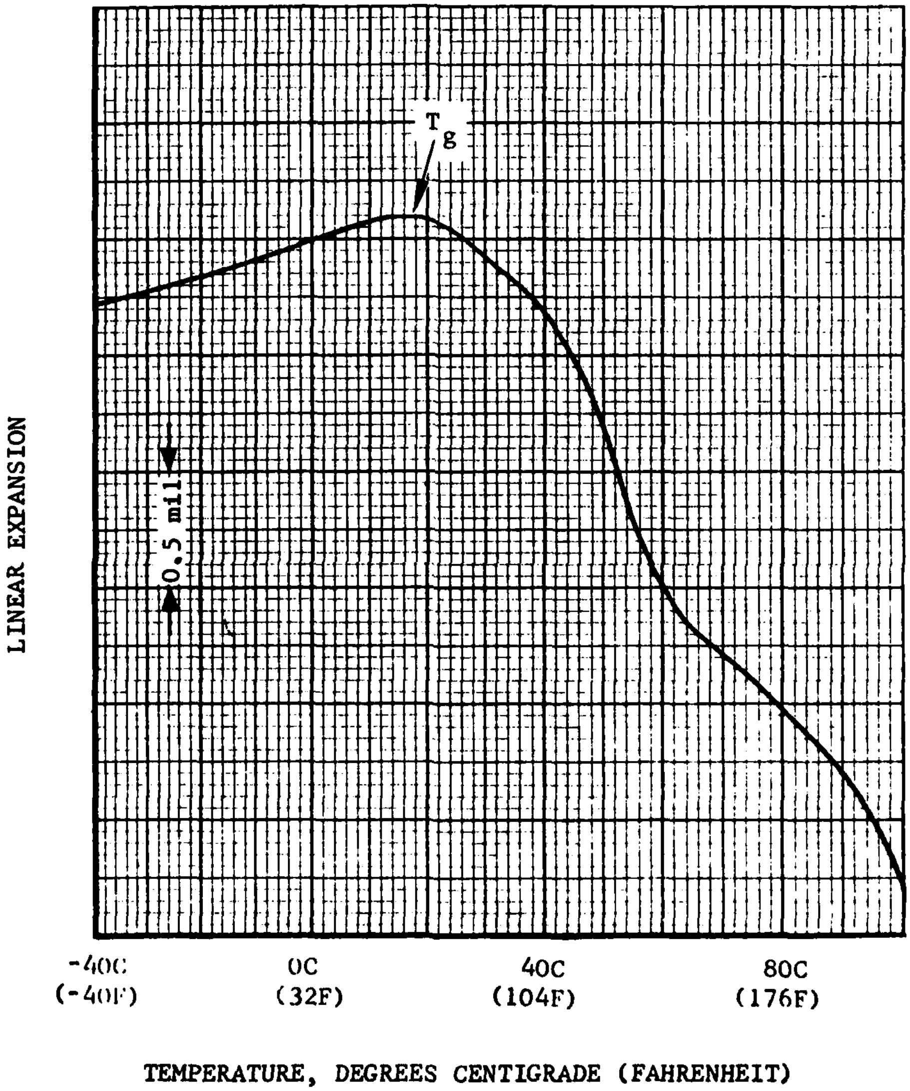


Figure 27. Thermal Mechanical Analysis of Versilok 513 Acrylic Adhesive Cured 24 Hours @ 24C (75F)

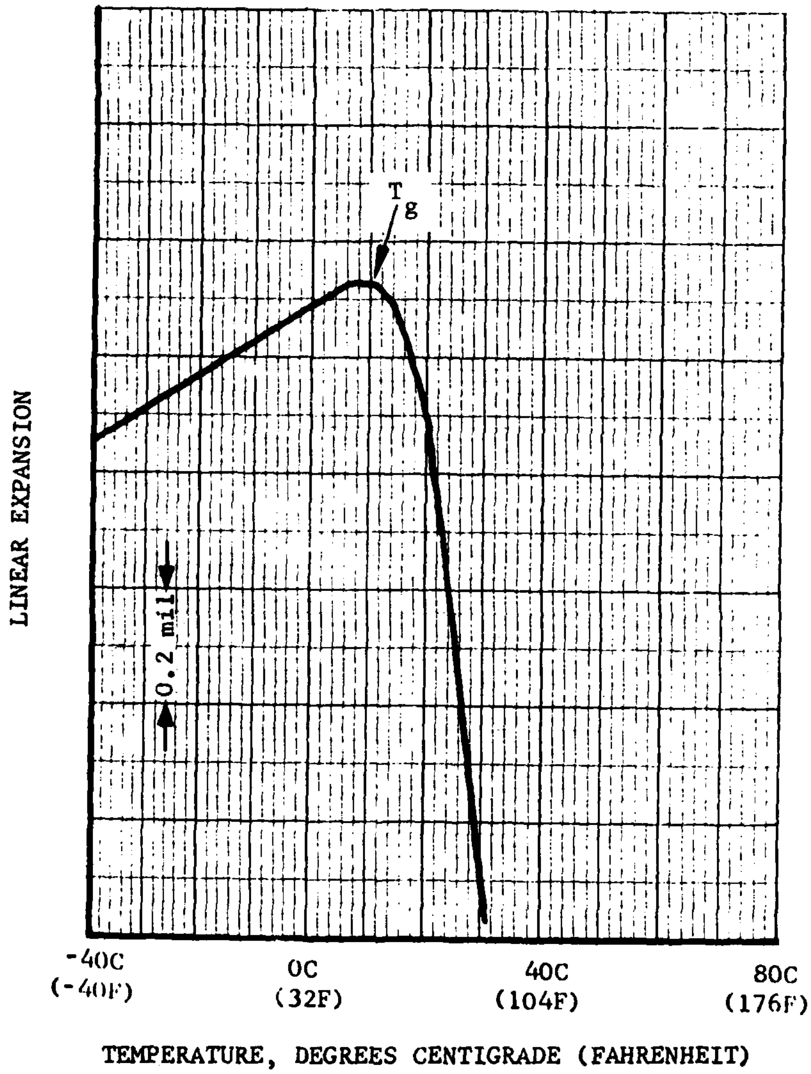


Figure 28. Thermal Mechanical Analysis of Rexite IMR-P2 Acrylic Adhesive Cured 24 Hours @ 24C (75F)

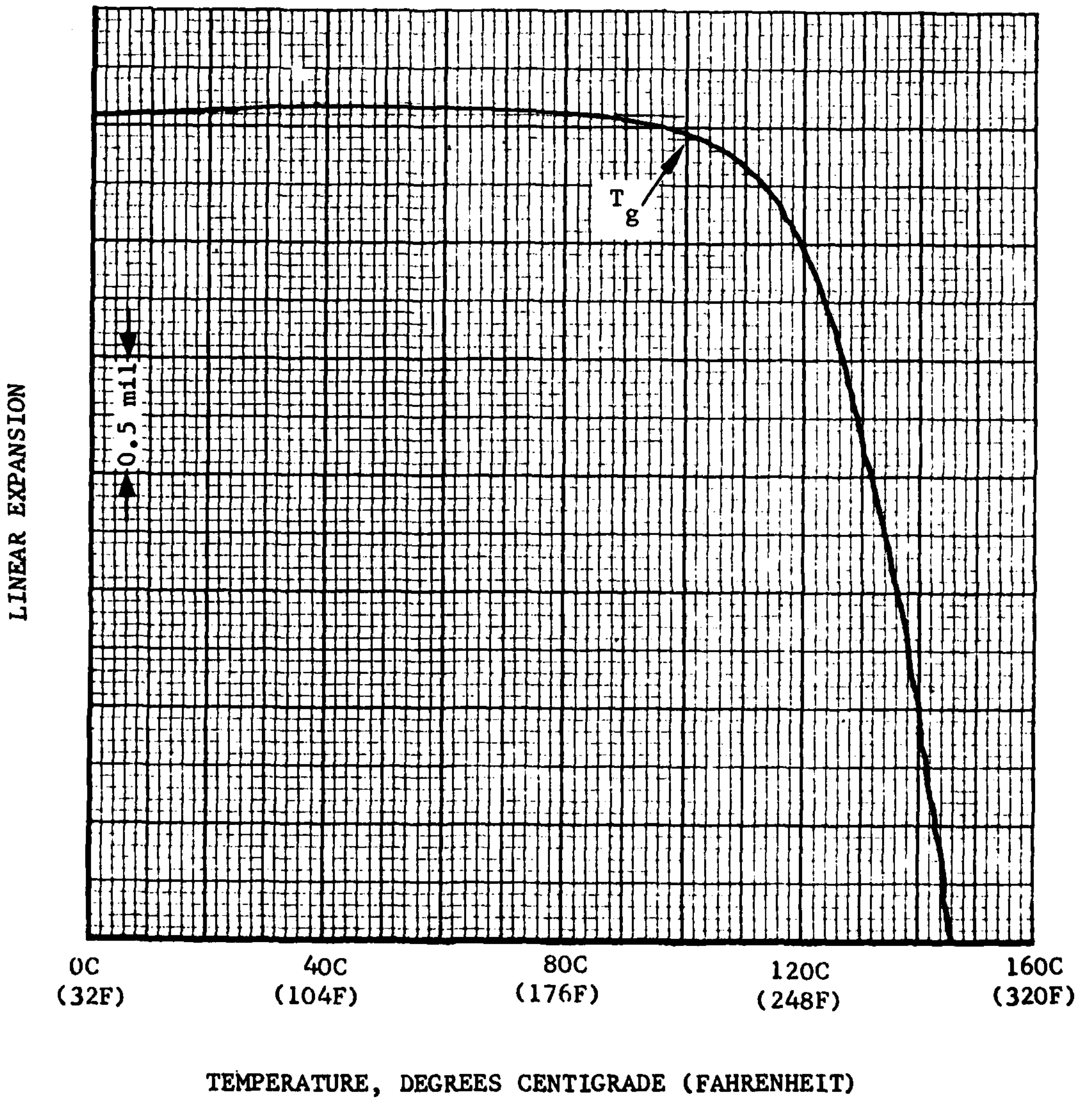


Figure 29. Thermal Mechanical Analysis of Weldmaster 3 Acrylic Adhesive Cured 24 Hours @ 24C (75F) and Postcured 1 Hour @ 100C (212F)

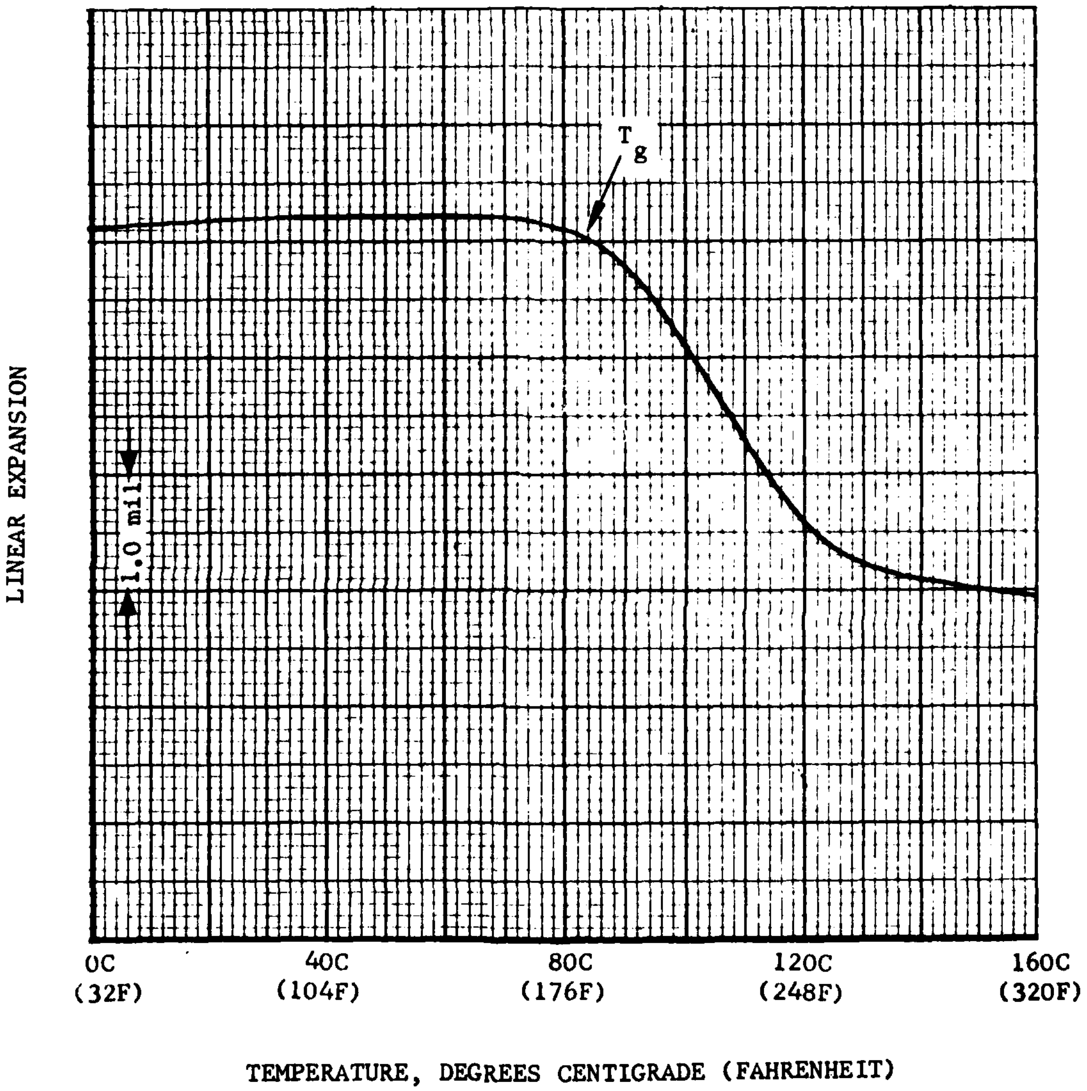


Figure 30. Thermal Mechanical Analysis of Versilok 513 Acrylic Adhesive Cured 24 Hours @ 24C (75F) and Postcured 1 Hour @ 75C (167F)

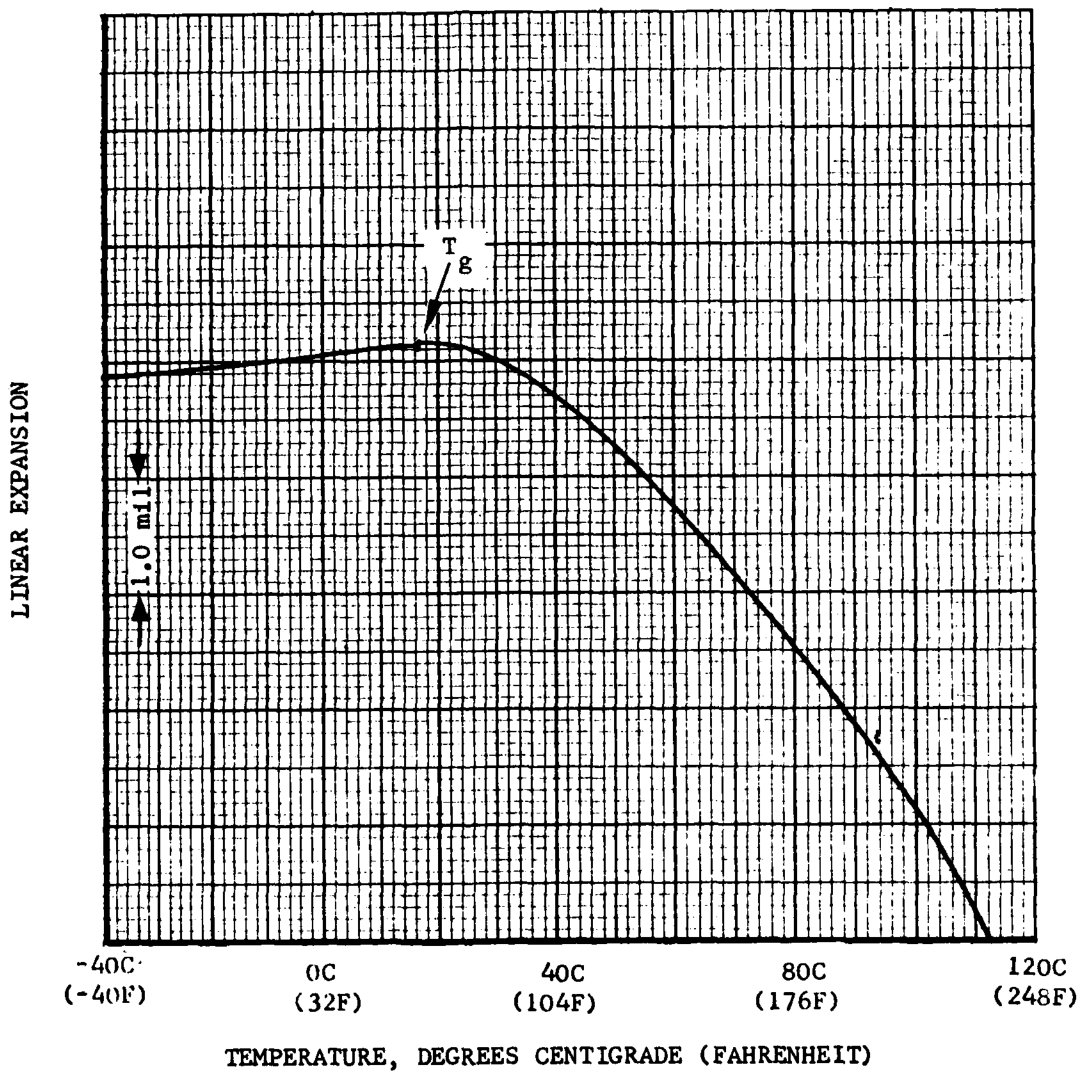


Figure 31. Thermal Mechanical Analysis of Rexite IMR-2 Acrylic Adhesive Cured 24 Hours @ 24C (75F) and Postcured 1 Hour @ 125C (257F)

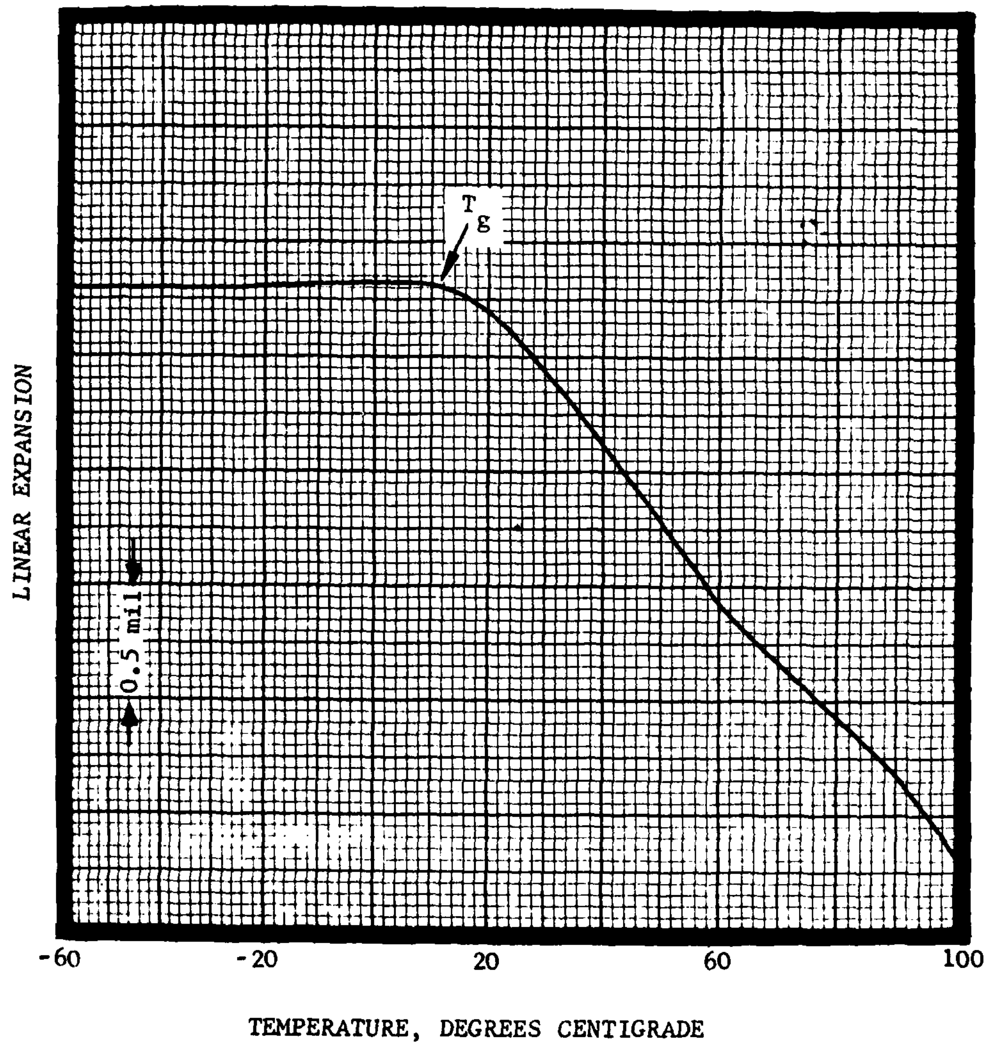


Figure 32. Thermal Mechanical Analysis of Hysol Acrylic Adhesive Cured At 24C (75F) and Postcured One Hour At 100C (212F).

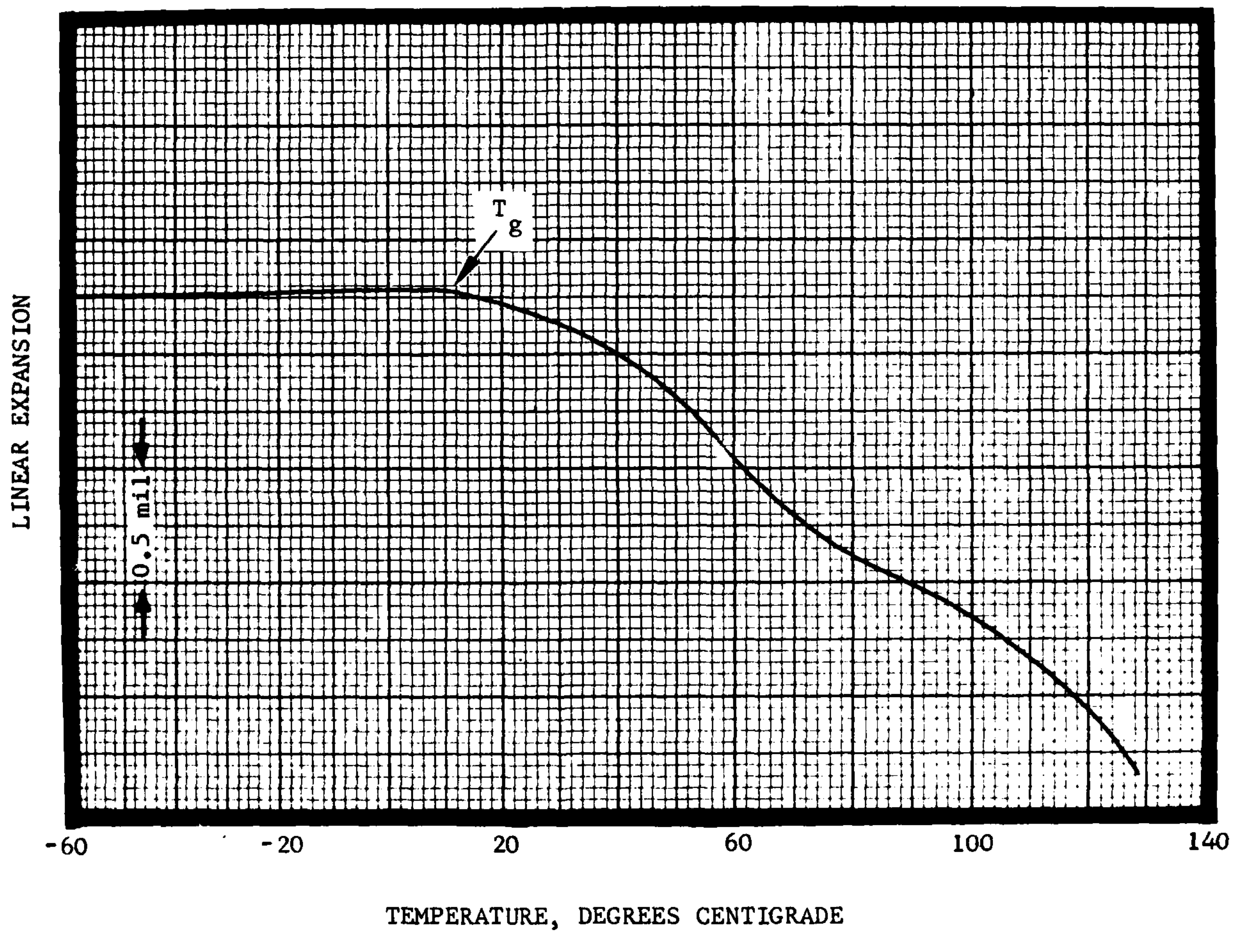


Figure 33. Thermal Mechanical Analysis of Hysol Acrylic Adhesive Cured At Ambient Temperature, 24C (75F).

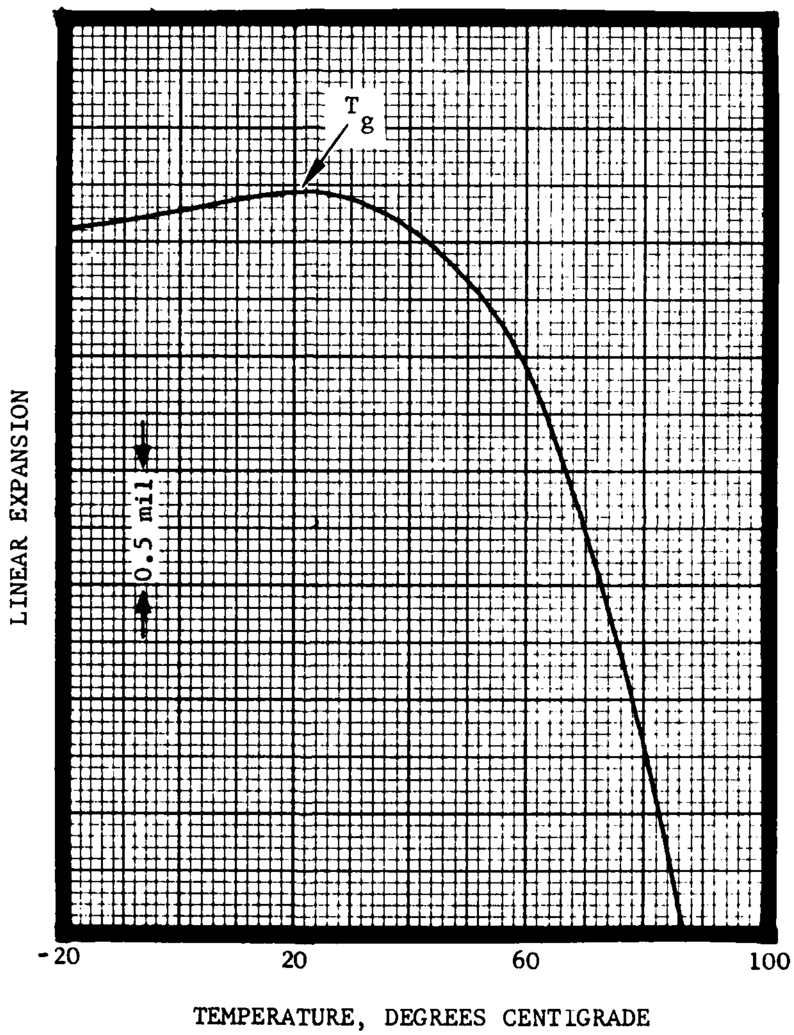


Figure 34. Thermal Mechanical Analysis of B.F. Goodrich Acrylic Adhesive Cured At Ambient Temperature, 24C (75F).

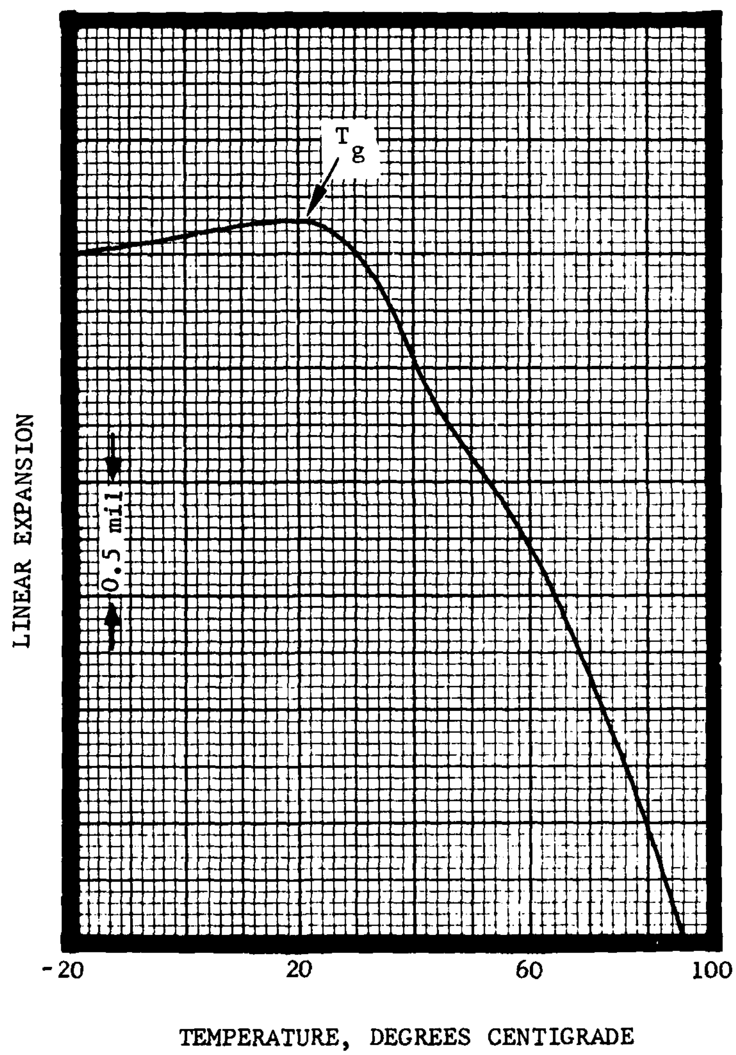


Figure 35. Thermal Mechanical Analysis of Bostik Acrylic Adhesive Cured At Ambient Temperature, 24C (75F).

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Conclusions

1. Instrumental analysis and mechanical testing indicate that commercially available epoxy, anaerobic, and acrylic room temperature curing adhesives will not meet the requirements for repair of damaged aircraft. They were not designed to meet the load and temperature conditions that adhesives used to repair damaged aircraft will experience.
2. Polymeric materials have been identified which, after formulation into adhesives, give good mechanical properties at 121C (250F) after cure at 24C (75F) for 72 hours. High molecular weight and high functionality epoxies look promising. A typical formulation is composed of a cresol novalac epoxy, Ciba Geigy's ECN 1299, and the triglycidyl ether of para-aminophenol, Ciba Geigy's 0510, and diethylene tetramine, a primary amine curing agent. This formulation gave lap shear strengths of 1400 psi at 121C (250F) after a room temperature cure. This is much higher than what can be obtained from commercial adhesives.
3. Using the high molecular weight, high functionality epoxy resin systems developed on this program, it appears possible to formulate a practical ambient temperature curing or moderate temperature curing adhesive which could be used in the near term for field repair.
4. Testing indicates that vinyl ester resins have potential as moderate temperature curing adhesives. A typical system composed of Dow's Derakane resin cured with methyl ethyl ketone peroxide had a glass transition temperature of 121C (250F) and a maximum moisture absorption of about one percent.

Recommendations for Future Work

1. Optimize the adhesive formulations which contain high molecular weight, high functionality epoxy resins:

A. Replace DETA curing agent with a resin/curing agent adduct that is non-volatile and non-toxic.

B. Incorporate CTBN type rubbers (B.F. Goodrich) into the formulation to maximize toughness in the adhesive.

C. Conduct extensive creep testing and mechanical testing of adhesive joints made with the optimized epoxy adhesives after moisture exposure.

D. Generate a backlog of data on graphite/epoxy bonded joints made with the optimized epoxy adhesives.

2. Develop a moderate temperature curing adhesive from the vinyl ester resin system.